Reactivity between Sn–Ag Solder and Au/Ni–Co Plating to Form Intermetallic Phases

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For the formation of micro joint not to melt by secondary reflow soldering, we tried to enhance the reactivity of Sn–Ag solder with Au/Ni–20Co plating. It was confirmed that the addition of Co in Ni and existence of Au plating effectively accelerated the reaction and the Sn–Ag solder completely transformed to the intermetallic compounds with a higher melting temperature.

Particularly, the addition of Co in Ni changed the interfacial reaction layer from Ni\textsubscript{3}Sn\textsubscript{4} to (Ni,Co)Sn\textsubscript{2} with higher diffusivity of Ni which enhanced the formation of the intermetallic phases. This process is expected to replace the packaging technology using high temperature solders.

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1. Introduction

In the electronics technology, high temperature solders are needed for chip to module joint in high end device. Conventionally, lead rich solders (Sn–90Pb and Sn–95Pb, for example) have been used as high temperature solders, but recent regulation against the usage of toxic lead requires the development of substitutional lead free solders.\textsuperscript{1)} At the present moment, however, compared with low or medium temperature solders, there is no critical substitution candidate in high temperature solder except for an expensive Au–20Sn solder.\textsuperscript{2)}

The purpose of this study is not to develop high temperature solder itself but to form high melting point joint composed of intermetallic compounds. Namely, although soldering was simply performed by using Sn–Ag solder, a positive enhancement of reaction between solders and Au/Ni–Co plating forms the micro joint comprised of intermetallic phases free from low melting temperature Sn. We have newly observed that the reaction between Sn–Ag solder and Au/Ni–Co plating is rapid enough to completely form the intermetallic phases even by a reflow soldering less than 573 K. In this paper, this alloying behavior was kinetically examined by the microstructural observation and thermal analysis of the joint. Besides, effect of the existence of Au or Co on the rapid alloy is discussed.

2. Experimental Procedure

Solder clad lid and base metal were bonded assuming the actual packaging of SAW filter. Solder lid was fabricated by cladding about 26\textmu m thick Sn–Ag solder on Ni sheet. Base metal was composed of Kovar sheet on which surface 5\textmu m thick Ni–20Co and 1\textmu m thick Au were plated. The structure and specification of the specimen in this study is shown in Fig. 1. As shown in this figure, the solder clad lid was bonded with Kovar plated Au/Ni–20Co by reflowing at 513 K in pressure at about 1.2 kPa.

In addition, in order to quantify the reactivity between Ni alloy and Sn–Ag solders, formation kinetics and mechanism of intermetallic phases were investigated for a simple diffusion couple of Ni alloy and Sn–Ag solder as shown in Fig. 2. For these couples, Reflow soldering was performed at a peak temperature of 513 and 553 K, for a holding time from

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_1.pdf}
\caption{Schematic illustration of cross section of Ni/Sn–Ag/Au/Ni–20Co plated Kovar joints.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_2.pdf}
\caption{Schematic illustration of cross section of Ni–xCo/Sn–Ag joint.}
\end{figure}
0 to $1.8 \times 10^3$ s in air atmosphere. Heating rate was varied from $3.3 \times 10^{-1}$ to $5.0 \times 10^{-1}$ K/s. The typical reflow thermal profile whose peak temperature was 513 K was shown in Fig. 3.

The microstructure of the joints was observed by optical microscope, scanning electron microscope (SEM) and transmission electron microscopy (TEM). The elemental distribution was evaluated with energy dispersive X-ray analysis (EDX), wavelength dispersive X-ray analysis (WDX) and electron probe microanalysis (EPMA). TEM sample was prepared by using focused ion beam (FIB). Differential scanning calorimetry (DSC) was carried out to examine the meling behavior at The heating rate of $3.3 \times 10^{-2}$–$3.3 \times 10^{-1}$ s$^{-1}$ in an argon flow atmosphere.

3. Results and Discussion

3.1 Influence of Au and Co on formation of intermetallic compound

In order to evaluate the effects of Au and Co quantitatively, alloying kinetics were investigated by microstructural observation for the joints of which solder thickness was expanded from 26 µm assuming actual packaging as shown in Fig. 1 to 100 µm as shown in Fig. 2. Figures 4 and 5 show the cross section of the Ni/Sn–Ag, Ni–20Co/Sn–Ag, Ni–20Co/Au/Sn–Ag or Ni/Au/Sn–Ag samples soldered at 513 K by various holding time up to 1.8 ks. Table 1 shows the results of quantitative WDX analyses for each phase in Figs. 4 and 5. For the samples which were jointed on Co free Ni sheet with Sn–Ag solders, $Ni_3Sn_4$ layer formed at Ni/Sn–Ag interface but the thickness hardly changed by holding at 513 K. On the other hand, for the samples which were jointed on Ni–20Co with Sn–Ag solders, $(Ni,Co)Sn_2$ layer was formed at Ni–20Co/Sn–Ag interface. Regardless to the existence of Au, it is confirmed that the addition of 20% Co to Ni changes the interfacial reaction layer from $Ni_3Sn_4$ layer to $(Ni,Co)Sn_2$ layer. Although the growth kinetics of the $(Ni,Co)Sn_2$ layer during holding at 513 K hardly changes with the $Ni_3Sn_4$ layer, formation of Ni–Co–Sn phase of which the atomic ratio is 18.9:4.1:77.0 was obviously confirmed even inside the solder. Since this phase was too small to identify by other methods, this phase is described as Ni–Co–Sn phase in this paper. As a reference, Haimovich and Kahn confirmed the formation of metastable $NiSn_3$, between Ni and Sn interface.

In the case of Au platted samples, pure Au plating completely disappeared during soldering. Just same to the joint without Au plating, the interfacial reaction layer changed from $Ni_3Sn_4$ layer to $(Ni,Co)Sn_2$ layer by Co addition although the thickness was about a half of that observed for the sample without Au plating. The formation of alloy phases was also confirmed inside the Sn–Ag solder and the composition of the alloy changed from $Ni_3Sn_4$ or Ni–Co–Sn phase to $(Au,Ni,Co)Sn_4$. Figures 6 and 7 illustrate the changes in the thickness of reaction layers and in the area ratio of intermetallic phases inside the solders as a function of holding time at 513 K, respectively. Area ratio of intermetallic phases (for example $(Au,Ni)Sn_4$ or $(Au,Ni,Co)Sn_4$) was
measured by image analyses of the back scattered electron images. At first for the reaction layers, although there are slight differences in their growth kinetics, the growth of reaction layers did not play a very important role on the rapid alloying of joints since the maximum thickness was only 10 \( \mu \)m. On the other hand, area fraction of intermetallic reached more than 50% for the Co containing joints (see dot line in Fig. 7) although area fraction became larger for the joints with Au than those without Au. Consequently, it can be concluded that the rapid alloying of joints is caused not by growth of interfacial reaction layer, but by the rapid alloying inside the solders. However, this rapid alloying behavior has no relation to the alloy phases formed inside the solder, since they are Ni–Co–Sn phase and \((\text{Au},\text{Ni,Co})\text{Sn}_4\) for the Ni–20Co/Sn–Ag and Ni–20Co/Au/Sn–Ag joints, respectively. What is common to these two joints is that interfacial reaction layer is composed of Ni–Co–Sn phase. Namely, the \((\text{Ni,Co})\text{Sn}_2\) layer itself does not grows so fast but enhances the alloying inside the solder. This interesting behavior of \((\text{Ni,Co})\text{Sn}_2\) layer is considered to be attributed to the lattice structure within which Ni and Co can easily diffuse toward solders.

### 3.2 Microstructure and thermal stability of Ni/Sn–Ag/Au/Ni–20Co joint

Figure 8 shows the joint microstructure of the Ni/Sn–Ag(26 \( \mu \)m)/Au/Ni–20Co assuming actual packaging of SAW filter brazed by various reflow peak temperature and holding time and the DSC thermal profiles of the corre-
sponding joints. Formation of an interfacial reaction layer was observed at the interface between Ni or Au/Ni–20Co and the Sn–Ag solder in all reflow conditions. Ni$_3$Sn$_4$ layer was formed at Ni/Sn–Ag interface, while an intermetallic compound of which molar ratio of Sn against the sum of Ni and Co is 1:2 was formed at Sn–Ag/Au/Ni–20Co interface. The intermetallic compound of which molar ratio of Sn against the sum of Au, Ni and Co is 1:4 was formed at the inside of solder. By taking account of the density of each phase, if Au and Ni–Co completely react with Sn to form (Au,Ni,Co)Sn$_4$ or (Ni,Co)Sn$_2$, it is estimated that about 30 µm thick Sn phase is completely consumed. According to the microstructure in Fig. 8, with increase of the holding time at reflow temperature, volume ratio of Sn decreased and finally Sn phase completely disappeared holding for $1.8 \times 10^3$ s at the peak temperature. This phenomenon was quantitatively confirmed by monitoring the variation of the endothermic peak corresponding to the melting of Sn in the DSC curve as shown in Fig. 8. It is generally known that a reaction layer formed at the interface between Ni and Sn–Ag is Ni$_3$Sn$_4$ layer. However, due to the barrier effect of this layer against the diffusion of Ni to solder, formation of intermetallic compound at inside of Sn–Ag solder was not occur as such even if holding time of peak temperature was extended. While, in this Ni/Sn–Ag/Au/Ni–20Co joint, much intermetallic compounds were formed and the amount of the heat of melting decreased. The microstructure of specimen in the case of heating until 553 K was similar to that in the case of holding at 513 K for $1.8 \times 10^3$ s, moreover, the endothermic peak decreased in the case of heating at
553 K than in the case of heating at 513 K. As these results, a rise in reflow peak temperature shows an effect same as an increase in holding time. Therefore, it is suggested that a variation of reflow thermal profile and the addition of Co or and existence of Au effectively accelerated the formation of intermetallic compound.

In order to investigate these alloying behavior, thermal analyses were performed at a lower heating rate of $3.3 \times 10^{-2}$ K/s for the Sn–Ag clad lid and Au/Ni–Co plated Kovar as shown in Fig. 9. DSC curve of the first run, Fig. 9(a), shows an endothermic peak at about 491 K corresponding to a melting peak of Sn–Ag eutectic reaction and a following exothermic peak. On the contrary, the DSC curve of the second run, Fig. 9(b) exhibited no peaks indicating the formation of micro joint with high melting temperature.

To study the intermetallic compound formation behavior at the each stage of heating, micro joint of a solder clad lid with Au/Ni–20Co plated Kovar heated to (A) 493 K, which is just after the endothermic reaction, or to (B) 513 K, which is just after the exothermic reaction, was prepared. In a specimen heated to 493 K, Ni$_3$Sn$_4$ or (Au,Ni)Sn$_4$ intermetallic phase was partially formed but most of the solders was composed of Sn as shown in Fig. 10(a). On the other hand, in a specimen heated to 513 K, Ni–Co–Sn phase of which the atomic ratio is 19.9:5.8:74.3 was formed in the joints to consume Sn almost all as shown in Fig. 10(b). From these results, it is obvious that Ni–Co–Sn phases were formed by an exothermic reaction between melted solder and Au/Ni–20Co plating.

Additionally, for the mechanical property of the joint, the Ni/Sn–Ag(26 mm)/Au/Ni–20Co joint has 10–20 MPa shear strength, almost the same level of solders.

From these, this process is available to the alternative to the packaging technology with high melting solders.

### 3.3 Lattice structure of (Ni,Co)Sn$_2$ interfacial reaction layer

There is not a ternary Co–Ni–Sn phase diagram available. Besides, there are no reports on the structure or formation mechanism of (Ni,Co)Sn$_2$ layer as far as we have investigated. For the binary systems, there is a tetragonal CoSn$_2$ structured intermetallic compound that in Co–Sn system although there is no NiSn$_2$ phase in Ni–Sn system.

Figure 11 shows the bright field TEM microstructure of (Ni,Co)Sn$_2$ layer formed at Ni–20Co/Sn–Ag joint. It was confirmed that (Ni,Co)Sn$_2$ exhibited a rectangular structure and uniaxially grew to the vertical direction against the interface. Figures 12(a) and (b) show electron diffraction patterns from two orientations for (Ni,Co)Sn$_2$ phase. Figure 13 shows X-ray diffraction angular spectra for a cross section of (Ni,Co)Sn$_2$ phase.

According to two diffraction patterns in Fig. 12, it was suggested that this (Ni,Co)Sn$_2$ layer has a cubic symmetry, which is absolutely different from tetragonal CoSn$_2$, and the
d-spacing of the (002) was 0.304 nm. On the other hand, as shown in X-ray diffraction of Fig. 13, the d-spacing of first peak was 0.3085 nm. Table 2 shows the comparisons of actually measured d-spacings with those calculated by assuming the (Ni,Co)Sn\(_2\) as a cubic with a lattice constant of 0.617 nm. As shown in Table 1, almost all actually measured d-spacings corresponded well with those of the calculated d-spacings. From these results, it was suggested that (Ni,Co)Sn\(_2\) phase had cubic system structure whose lattice constants were 0.617 nm.

Diffusion in the intermetallic compound is generally known to be slower than that in the metal because the

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Fig. 11 TEM image of (Ni,Co)Sn\(_2\) phase.

Fig. 12 Diffraction patterns and key diagrams obtained from Fig. 11.
effective jump sites of atoms are limited due to the ordered structure of intermetallic compounds. In this sense, compared with complex monoclinic Ni₃Sn₄ structure, it is interpreted that Ni and Co can easily diffuse through the simple cubic (Ni,Co)Sn₂ with more atom jumping sites. It was suggested that (Ni,Co)Sn₂ was effective in diffusion of Ni or Co.

4. Conclusions

In this work, the effect of the addition of Co in Ni sheet and the existence of Au plating and reflow thermal profile on the joints with Sn–Ag solders were evaluated. The main results obtained are as follows.

(1) It is possible that the joints with Co contained sample were not melting at secondary reflow process by controlling reflow thermal profile. This process is available to replace the packaging technology with high temperature solders.

(2) Regardless to the existence of Au, the addition of 20% Co to Ni changed the interfacial reaction layer from Ni₃Sn₄ layer to (Ni,Co)Sn₂ layer. Formation of Ni–Co–Sn or (Au,Ni,Co)Sn₄ inside the solders was also confirmed for all of the joints but Ni/Sn–Ag joints. The more holding time of reflow peak temperature increased, the more this phase was formed.

(3) Holding the joints at 513 K developed the alloying of the joints. The growth of interfacial reaction layers did not play a very important role on the rapid alloying of joints since the maximum thickness was only 10 μm. The rapid alloying of joints is rate controlled by the alloying inside the solders and especially the alloying rate was fast for the Co containing joints.

(4) The important issue for the alloying is the change in interfacial reaction layer from Ni₃Sn₄ to (Ni,Co)Sn₂ by Co addition. It was confirmed that the (Ni,Co)Sn₂ has a simple cubic lattice structure within which Ni or Co can easily diffuses to solders.

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REFERENCES