Formation of Intermetallic Compounds in the Ni Bearing Lead Free Composite Solders

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Quaternary Sn–Ag–Cu–Ni composite solders were made with several different ratios of Cu/Ni to study the effect of Cu/Ni on the type of intermetallic compound phase at the joint interface. The eutectic solders of Sn–3.5Ag and Sn–3.5Ag–0.7Cu (numbers are all in mass% unless specified otherwise) were used as references together with the ternary composite solder of Sn–3.0Ag–7.0Cu tested previously. When the ratio of excess Cu/Ni alloyed in the original composite solder was 7 : 3, 6 : 4 and 5 : 5, the reinforcing intermetallic compound (IMC) was (Cu,Ni)₆Sn₅. When the ratio was Cu : Ni = 3 : 7, both phases of (Cu,Ni)₆Sn₅ and (Ni,Cu)₃Sn₄ showed up while only the (Ni,Cu)₃Sn₄ phase was observed in the solder with a Cu : Ni ratio of 1 : 9. For the interfacial reaction of the eutectic Sn–3.5Ag–0.7Cu with the rolled Ni substrate, the thick (Cu,Ni)₆Sn₅ layer was formed on the thin (Ni,Cu)₃Sn₄ layer. The addition of Ni was effective to suppress the formation of the thick (Cu,Ni)₆Sn₅ IMC. When the (Cu_xNi_{1–x})₆Sn₅ IMC layer was formed, the value of *x* was larger than 0.6 while for the case of (Ni_yCu_{1–y})₃Sn₄ the value of *y* was larger than 0.8. The addition of Ni enhanced the bonding properties and retarded the growth of IMC. In the Ni bearing composite solder, there was no significant sedimentation of reinforcing particles during reflow, which took place commonly in the other composite solders. Wettability and mechanical properties of the Ni bearing solders were also compared.

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1. Introduction

Electronic devices such as computers and cellular phones have become thinner and smaller with more complicated functions. Miniaturization of these electronic devices demands better reliability of the solder joint, because a small solder bump experiences harsh conditions caused by increased heat emission per unit size. One approach to improve reliability is using a composite solder, which consists of a solder matrix and reinforcements. Composite solders are known to have good reliability because the reinforcing particles can suppress grain-boundary sliding, IMC formation, grain growth, and furthermore, uniformly redistribute stress.^{1–14)}

According to the conventional manufacturing processes of composite solders,^{1–5)} solder pastes or solder powders are intentionally mixed with Cu₆Sn₅ reinforcements. In other methods,^{6–12)} the solder is mixed with metal powders, such as Ag, Cu and Ni, and reflowed to form IMC particles inside the solder matrix. However, the latter methods enable only the surface area of metal powders to react with mostly Sn of the Sn-rich solder to form intermetallic particles while the former methods are not practiced these days.

The authors devised innovative methods for fabricating composite solders, which consisted of the Sn–Ag solder matrix and the Cu₆Sn₅ particles.^{13,14)} Composite solders were prepared by a novel *in-situ* process, solidification and deformation. The molten solder with the same composition of the resultant composite is rapidly solidified as thin sheet. During solidification, primary IMC dendrites form in the solder matrix and they are crushed into fine particles and redistributed by way of plastic working. IMC reinforcements made by this method were much finer than those by the

conventional manufacturing method. Thus, it was motivated to expand the method to incorporate Ni containing IMCs as well as Cu bearing IMCs.

In this work, Sn–Ag based solders reinforced with (Cu,Ni)₆Sn₅ and (Ni,Cu)₃Sn₄ particles were manufactured. These solders and their joints with Cu and Ni were studied. The interfacial phase and microstructure, the joint strength after soldering and aging were investigated with an emphasis on the effect of variation in the ratio of Cu/Ni.

2. Experimental Procedures

Composite solders were rapidly solidified. Primary IMC dendrites formed in the solder matrix during solidification were crushed into fine particles and redistributed by way of rolling or drawing. The details of fabrication are available in earlier publications.^{13,14)} The discs punched out of the rolled strip are remelted in hot oil to be spheroidized, thereby becoming solder balls with an average diameter of 630 μm.

Quaternary Sn–Ag–Cu–Ni composite solders were made with several different ratios of Cu/Ni. The ratios of Cu/Ni (in mass%) in excess of the quaternary eutectic composition to be determined later in this study are as follows: 0.11, 0.43, 1.0, 1.5 and 2.33 (Cu : Ni = 1 : 9, 3 : 7, 5 : 5, 6 : 4 and 7 : 3) and additional Cu and Ni elements above the eutectic composition were assumed to form Cu₆Sn₅ or Ni₃Sn₄ respectively, and the total volume of IMC was aimed at 15 volume%. Their compositions are shown in Table 1. The binary eutectic non-composite solder of Sn–3.5Ag (solder A) and the ternary near-eutectic non-composite solder of Sn–3.5Ag–0.7Cu (solder B), were used as references together with the previous ternary composite solder of Sn–3.0Ag–7.0Cu (solder C).^{13,14)}

For the substrates, Cu and Ni were used in the form of a printed circuit board (PCB) and a rolled plate. Metal plates

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Table 1 Composition and types of solders.

Solders	Composition (in wt%)	Ration of Cu/Ni* (Cu : Ni)	Remarks
A	Sn-3.5Ag		Sn-Ag eutectic
B	Sn-3.5Ag-0.7Cu		Sn-Ag-Cu eutectic
C	Sn-3.0Ag-7.0Cu		Sn-Ag-Cu composite
D	Sn-3.2Ag-0.6Cu-0.7Ni		Sn-Ag-Cu-Ni eutectic
E	Sn-2.7Ag-1.1Cu-4.8Ni	0.11 (1 : 9)	Sn-Ag-Cu-Ni composite
F	Sn-2.7Ag-2.2Cu-4.1Ni	0.43 (3 : 7)	Sn-Ag-Cu-Ni composite
G	Sn-2.7Ag-3.8Cu-3.6Ni	1.0 (5 : 5)	Sn-Ag-Cu-Ni composite
H	Sn-2.8Ag-4.8Cu-2.9Ni	1.5 (6 : 4)	Sn-Ag-Cu-Ni composite
I	Sn-2.8Ag-5.1Cu-2.5Ni	2.33 (7 : 3)	Sn-Ag-Cu-Ni composite

(Cu/Ni*: projected Cu/Ni ratio in excess of the quaternary eutectic composition)

Fig. 1 Reflow temperature profile.

were mechanically polished before reflow. Rosin mildly activated (RMA) flux was painted on the substrate and it was reflowed according to the temperature profile shown in Fig. 1. The solder joints were then isothermally aged at 120°C for up to 36 d.

To study the interfacial microstructure, each solder joint was vertically cut and cold mounted. They were then polished through a 1 μ m diamond. The interface was examined using back scattered scanning electron microscopy (SEM) operated at 25 kV and the compositions of the interfacial IMC were measured by energy dispersive X-ray spectroscopy (EDX: EDAX DX-4eDX PhiZAF System version 2.11) operated at 20 kV. The spatial resolution was approximately a 1 μ m diameter area around the target point and the compositions were determined by an average of ten point measurements. The phases formed at the interface and inside the composite were identified by the X-ray diffraction (XRD) analysis and the layer thickness of IMCs was obtained as the averaged value by area of SEM micrographs.

The differential scanning calorimetry (DSC) analysis was employed to measure the eutectic temperature of the quaternary Sn-Ag-Cu-Ni solder. It was put into aluminum pan and the thermal scan was carried out at the heating rate of 1°C/min from 40 to 280°C under nitrogen. The solder joint strength was measured using a Dage 2400 ball shear tester. The jig speed was 100 μ m/s and the jig height was 10 μ m from the bottom while the load applied was 50 g. Wetting angles were measured using solder foils (10 mm diameter) reflowed on the rolled Cu substrate.

Table 2 List of sources of thermodynamic parameters.

Binary system	Ref.	Binary System	Ref.
Ag-Cu	16)	Cu-Ni	19)
Ag-Ni	17)	Cu-Sn	20)
Ag-Sn	18)	Ni-Sn	21)

All the ternary and quaternary systems are extrapolated from the binary thermodynamic descriptions.

Fig. 2 Heat flow versus temperature curve for the Sn-Ag-Cu-Ni eutectic solder, D.

3. Results and Discussion

To determine the exact eutectic composition of the quaternary Sn-Ag-Cu-Ni solder, the phase equilibria calculations were made using a Thermo-Calc program.¹⁵⁾ Table 2 lists up the references of the thermodynamic description and parameters of the binary systems used in this study.¹⁶⁻²¹⁾ All the ternary and quaternary systems were extrapolated from binary thermodynamic descriptions only. The quaternary eutectic reaction was calculated to occur at Sn-3.24Ag-0.64Cu-0.75Ni and 216°C. To confirm the calculations, the DSC analysis of the solder specimen with the same composition (solder D) was performed. The curve of heat flow versus temperature is shown in Fig. 2, which shows only one sharp peak corresponding to the invariant reaction. No other phase change was observed. The onset temperature was 216.25°C, almost the same as the calculated one. Thereby, in this work, Sn-3.24Ag-0.64Cu-0.75Ni was taken as the quaternary eutectic composition.

Even if the calculated temperature is very close to the onset

Fig. 3 Microstructure of the (Cu,Ni)₆Sn₅ IMC reinforced Sn–Ag–Cu–Ni composite solder, I.

Fig. 4 Microstructure of (Ni,Cu)₃Sn₄ IMC reinforced Sn–Ag–Cu–Ni composite solder, E.

Table 3 Reinforcing IMC types and composition according to Cu/Ni ratio above eutectic composition.

Composite Solders	Ratio of Cu : Ni alloyed (aimed)	Type of IMC and Composition
E	1 : 9	≈(Ni _{0.91} , Cu _{0.09}) ₃ Sn ₄
F	3 : 7	≈(Ni _{0.80} , Cu _{0.20}) ₃ Sn ₄ + (Cu _{0.55} , Ni _{0.45}) ₆ Sn ₅
G	5 : 5	≈(Cu _{0.53} , Ni _{0.47}) ₆ Sn ₅
H	6 : 4	≈(Cu _{0.61} , Ni _{0.39}) ₆ Sn ₅
I	7 : 3	≈(Cu _{0.72} , Ni _{0.28}) ₆ Sn ₅

temperature of the DSC analysis it is notable that there are some uncertainties in the eutectic composition, because the undercooling is significant for the Sn-based alloy and the DSC result is not that sensitive to discern two very close reactions. Furthermore, the thermodynamic calculations have been made using binary systems only. No ternary or quaternary descriptions were included.

Figure 3 shows the SEM micrograph of the as-cast solder I (Cu : Ni = 7 : 3). The area marked by number 1 shows the (Cu,Ni)₆Sn₅ reinforcing dendrites. The region 2 with dark contrast is composed of primary Sn dendrites and the region 3 refers to the eutectic-type structure of Sn, Ag₃Sn and (Cu,Ni)₆Sn₅ phases. To investigate which kind of reinforcing intermetallic phases are formed in the matrix, the XRD analysis were conducted along with EDX analysis. When the ratio of excess Cu/Ni alloyed in the original composite solder was 7 : 3, 6 : 4 and 5 : 5, the reinforcing IMC phase was (Cu,Ni)₆Sn₅. The compositions of IMC particles are shown in Table 3. When the ratio was Cu : Ni = 3 : 7, both phases of (Cu,Ni)₆Sn₅ and (Ni,Cu)₃Sn₄ showed up while only the (Ni,Cu)₃Sn₄ phase was observed in the solder E (Cu : Ni = 1 : 9).

The phase formation in the as-solidified Sn–Ag–Cu–Ni quaternary alloys has been also reported by the Chen group.^{22,23)} The formation of (Cu,Ni)₆Sn₅ and (Ni,Cu)₃Sn₄ is mostly affected by the ratio of Cu/Ni but not much by the added amount of Ag.

The microstructure of the (Ni,Cu)₃Sn₄ reinforced composite solder E (Cu : Ni = 1 : 9) is shown in Fig. 4. The particles with dark contrast are (Ni,Cu)₃Sn₄ IMCs. The solubility limit of Ni in (Cu,Ni)₆Sn₅ is around 0.45–0.5 based

(a)

(b)

Fig. 5 Cross-sectional micrographs of (a) Sn–Ag–Cu composite solder, C and (b) Sn–Ag–Cu–Ni composite solder, H. Particle-free zone is observed at the upper part of solder C (a) while it is absent in solder H (b).

on Table 3. Even though the (Ni,Cu)₃Sn₄ primary dendrites were not detected in the solder G (Cu : Ni = 5 : 5), there is a possibility for (Ni,Cu)₃Sn₄ to form, because the composition of the solder G is located almost at the end of solubility limit of Ni. Therefore in this study, the solder H (Cu : Ni = 6 : 4) that has the highest Ni content without forming (Ni,Cu)₃Sn₄ was selected as an exemplary (Cu,Ni)₆Sn₅ reinforced Sn–Ag–Cu–Ni composite.

In the ternary composite solder C, particle sedimentation was observed as seen in Fig. 5. At the upper part of the composite solder ball, the particle-free zone was found while this behavior was not observed in the composite solder H (Cu : Ni = 6 : 4). In the solder H, the IMC phase was $(\text{Cu,Ni})_6\text{Sn}_5$ while it was Cu_6Sn_5 in the case of solder C (no Ni containing). The particle-free zone seems to result from gravitational sedimentation. The densities of the eutectic Sn–Ag–Cu solder and the Cu_6Sn_5 phase are 7500 and 8200 kg/m³, respectively.^{24,25} Because Cu_6Sn_5 is heavier than the solder matrix, it tends to sink down to the substrate during reflow. But there was no significant sedimentation in the Sn–Ag–Cu–Ni composite solder H, because the Ni substitution makes $(\text{Cu,Ni})_6\text{Sn}_5$ lighter in weight. The atomic weight of Cu and Ni are 63.55 and 58.70 g/mol, and their radii are 0.157 and 0.162 nm. This difference may not be large enough to change the density of $(\text{Cu,Ni})_6\text{Sn}_5$. An analysis by Pauling²⁶) may be used to assess the nature of bonding in IMC. Cu_6Sn_5 has a hexagonal NiAs ($B8_1$) type structure with $a = 0.419$ nm and $c = 0.509$ nm. The interatomic distance of fractional bonding materials such as Cu_6Sn_5 is varied by the bonding number n and the valence of elements. The substitution of Ni can change the lattice parameter and density, even though the densities of Ni and Cu are not much different. Based on this reasoning, there was no remarkable reinforcement sedimentation in the solder H.

The ball shear strength is shown as a function of aging time in Fig. 6. Black, gray and white symbols represent Sn–Ag–Cu–Ni composite (solder H), Sn–Ag–Cu composite (solder C) and Sn–Ag monolithic (solder A) solders, respectively, while circle and square symbols denote reflows on Ni and Cu substrates. The Sn–Ag–Cu–Ni composite solder has higher shear strength than the other solders, especially, on the Ni substrate. In other words, on the Ni substrate, the shear strength decreased most slowly with aging time. As the Cu addition into Sn–Ag hardens the solder matrix and enhances bonding properties on the Cu substrate,^{25,27,28}) the

Fig. 6 Variation of ball shear strength with aging time.

Fig. 7 Variation of IMC layer thickness with aging time.

addition of Ni into Sn–Ag–Cu is also expected to increase the bonding strength on the Ni substrate. The hardening effect may come together with the increased ductility. It is generally known that at low strain rate and displacement the composite solders are more ductile than the monolithic solders.^{1–14}) Then, the Ni bearing composite solders are supposed to increase reliability.

The growth of the IMC layer is plotted as a function of aging time in Fig. 7. On the Cu substrate, the growth of IMC was fast in the binary monolithic solder A, and the solders C and H showed similar behavior. The growth of IMC on the Ni substrate was slow compared to that on the Cu substrate. This behavior persisted in all the three solders of A, C and H, and the growth rate was more or less same. It is highly likely that the IMC was based on Ni_3Sn_4 in all the three solder joints with Ni and thus their growth rate and the buildup of the IMC was similar. The IMC layers are more brittle than the solder matrix and thus a thick IMC layer can be a site of mechanical weakness causing failure of the joint. Therefore, retarded growth of the IMC layer is very important to improve the solder joint reliability. It was reported that the growth of Cu_6Sn_5 in the Sn–Ag–Cu solder is slower than that of the Sn–Ag solder on the Cu substrate because of the reduced concentration gradient of Cu into the solder matrix and the decreased flux of Cu in turn.^{4,5,29}) In a similar way, it is expected that the growth of Ni_3Sn_4 can also be retarded in the Ni bearing composite solder on the Ni substrate.

The cross-sectional SEM micrographs of the interfacial reaction of Sn–Ag–Cu/rolled Ni after reflow with different Cu concentrations are shown in Figs. 8(a) and (b). The composition of the solder is Sn–3.5Ag–0.4Cu in Fig. 8(a) and Sn–3.5Ag–0.7Cu (solder B) in Fig. 8(b). An additional difference to be noted here is the use of a rolled Ni plate rather than PCB to investigate the effect of the substrate conditions. The thick $(\text{Cu,Ni})_6\text{Sn}_5$ layer was formed on the

(a)

(a)

(b)

(c)

Fig. 8 Cross-sectional micrographs of the interface between the Ni substrate and (a) Sn-3.5Ag-0.4Cu (composition not listed in Table 1), (b) Sn-3.5Ag-0.7Cu (solder B) and (c) XRD pattern of the interfacial IMC layer in solder B as-reflowed condition.

thin $(\text{Ni,Cu})_3\text{Sn}_4$ layer in both cases. Because Cu_6Sn_5 grows faster than Ni_3Sn_4 , the formation of the thick $(\text{Cu,Ni})_6\text{Sn}_5$ layer surely decreases the solder joint reliability. Its formation was verified by XRD in Fig. 8(c). Its peak showed up simultaneously with peaks of $(\text{Ni,Cu})_3\text{Sn}_4$ and Ni. When the solder B (Sn-3.5-0.7Cu) was reflowed on the plated Ni PCB, not on the rolled Ni substrate, the $(\text{Cu,Ni})_6\text{Sn}_5$ IMC layer was not observed but only the Ni_3Sn_4 layer showed up. The difference seems to have originated from the different condition of the Ni substrate, whether rolled or plated, even if the reason is not clear yet. When the solder of Sn-3.5Ag-

(b)

Fig. 9 (a) Cross-sectional micrograph of the interface between the Ni substrate and Sn-3.2Ag-0.6Cu-0.7Ni (solder D) and (b) XRD pattern of the IMC layer as-reflowed condition.

0.4Cu [tested in Fig. 8(a)] was reflowed with the plated Ni, the same result was obtained.

The interfacial reaction of the eutectic Sn-3.2Ag-0.6Cu-0.7Ni (solder D) with the Ni substrate after reflow is shown in Fig. 9(a). The addition of Ni to solder B suppressed the formation of $(\text{Cu,Ni})_6\text{Sn}_5$, leaving the IMC layer composed of only $(\text{Ni,Cu})_3\text{Sn}_4$. The XRD peaks of $(\text{Ni,Cu})_3\text{Sn}_4$ appeared with the peaks of the Ni substrate in Fig. 9(b). The addition of Ni was effective to suppress the formation of the thick $(\text{Cu,Ni})_6\text{Sn}_5$ IMC and, therefore, the Ni bearing solder can enhance the solder joint reliability in this sense.

The compositions of the IMC layer were carefully measured by EDX, nonetheless, they are subject to an uncertainty of a few atomic percent because the $(\text{Ni,Cu})_3\text{Sn}_4$ layer was very thin. When the $(\text{Cu}_x\text{Ni}_{1-x})_6\text{Sn}_5$ IMC layer was formed, the value of x was larger than 0.6 while for the case of $(\text{Ni}_y\text{Cu}_{1-y})_3\text{Sn}_4$ the value of y was larger than 0.8. This is similar to Table 3 and the stable composition (in mass%) range of both IMC phases is shown in Fig. 10.

Generally, the phase formation in an as-solidified alloy and an equilibrated alloy is different even if they are of the same composition. The alloy examined in this study is somewhat between the two situations. The cooling rates of the alloys examined are 15°C/s for the casting condition and 1°C/s for the reflow test. In spite of a large difference in the cooling rate employed, there was no remarkable difference in phase formation observed.

It was reported that the joint reaction of Sn-Cu/Ni and Sn-Ni/Cu, and the heat treatment of Sn-Cu-Ni alloys result in

Fig. 10 Stable composition (in mass%) ranges of $(\text{Cu,Ni})_6\text{Sn}_5$ and $(\text{Ni,Cu})_3\text{Sn}_4$ after reflow or casting.

formation $(\text{Cu,Ni})_6\text{Sn}_5$ and/or $(\text{Ni,Cu})_3\text{Sn}_4$ IMCs depending on the temperature and exact compositions, because both IMC phases have an extensive ternary solubility.³⁰⁻³⁴⁾ The stable composition range of IMCs in the Sn–Ag–Cu–Ni quaternary solder (Fig. 10) was close to the reported Sn–Cu–Ni ternary isotherm.^{32,34)} In the quaternary system, Sn–Ag–Cu–Ni, Ag did not exert an effect on the solubility and stoichiometry of Cu_6Sn_5 and Ni_3Sn_4 . However $(\text{Cu,Ni})_3\text{Sn}$ and Ni_3Sn_2 were not observed in this study due to the relatively lower contents of Cu and Ni and shorter aging time. Based on this information it is possible to expect the type of the IMC phase as a function of Cu and Ni concentrations, after reflow and casting.

The wetting properties of the eutectic Sn–Ag–Cu–Ni (solder D) were compared with the eutectic Sn–Ag–Cu (solder B) in Fig. 11. The wetting angle, 15° , of the Ni bearing solder D in Fig. 11(b) was almost the same as that of the Sn–Ag–Cu solder B. Typically the electronics industry involves multiple-pass solder operation in which solders are reflowed several times. In such operation, the wettability of the solder is extremely important. Especially, the addition of Ni may decrease the wetting properties but there was no significant decrease in wettability in this study, which is promising after all.

4. Summary

Quaternary Sn–3.24Ag–0.64Cu–0.75Ni eutectic composition was calculated using a Thermo-Calc program. Many advantages of Ni bearing solder were introduced. In the Ni bearing composite solder, there was no significant sedimentation of reinforcing particles during reflow, which took place commonly in the other composite solders. Ni addition enhanced the bonding properties and retarded the IMC growth. The wetting angle of the Ni bearing solder was almost the same as that of the Sn–Ag–Cu.

When the ratio of excess Cu/Ni alloyed in the original

(a)

(b)

Fig. 11 Cross-sectional micrographs of (a) Sn–Ag–Cu eutectic solder, B and (b) Sn–Ag–Cu–Ni eutectic solder, D on the Cu substrate after wetting test.

composite solder was 7 : 3, 6 : 4 and 5 : 5, the reinforcing intermetallic compound (IMC) was $(\text{Cu,Ni})_6\text{Sn}_5$. When the ratio was Cu : Ni = 3 : 7, both phases of $(\text{Cu,Ni})_6\text{Sn}_5$ and $(\text{Ni,Cu})_3\text{Sn}_4$ showed up while only the $(\text{Ni,Cu})_3\text{Sn}_4$ phase was observed in the solder with a Cu : Ni ratio of 1 : 9.

For the interfacial reaction of the eutectic Sn–3.5Ag–0.7Cu with the rolled Ni substrate, the thick $(\text{Cu,Ni})_6\text{Sn}_5$ layer was formed on the thin $(\text{Ni,Cu})_3\text{Sn}_4$ layer. The addition of Ni was effective to suppress the formation of the thick $(\text{Cu,Ni})_6\text{Sn}_5$ IMC. When the $(\text{Cu}_x\text{Ni}_{1-x})_6\text{Sn}_5$ IMC layer was formed, the value of x was larger than 0.6 while for the case of $(\text{Ni}_y\text{Cu}_{1-y})_3\text{Sn}_4$ the value of y was larger than 0.8. Based on this information it is possible to expect the type of the IMC phase as a function of Cu and Ni concentration, after reflow and casting.

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