Effect of Ni or Co Addition to Sn-Ag Solder on Microstructure and Joint Strength at Interface

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Among various lead-free alloys, Sn-Ag(-Cu) system solders are considered the most promising lead-free solders for both wave and reflow soldering technology. Moreover, to improve the characteristics of lead-free solders, the effect of the addition of minor elements to lead-free solders on the properties of solder and interfacial reactions have been studied. The purpose of this research was to investigate the addition of Ni or Co to the Sn-Ag solder on the microstructure and the joint strength of the interface with metallization layer of the substrate. As a metallization layer of the substrate, bare Cu and electroless Ni-P plating were used. For the reflow process, test samples were heated in a radiation furnace at 523 K for 60 s, and for the aging process, some samples were heat-treated in an oil bath at 423 K for 168 h, 504 h and 1008 h. Results show the addition of Ni or Co was effective for the IMC formation and growth at the interface with a Cu pad during reflow and aging process, and the addition of Co, except Ni, affected the pull strength of the solder joint with electroless Ni-P plating during aging process.

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1. Introduction

Soldering is widely used to connect electronic devices to printed circuit boards. The EU RoHS directive dictated that products sold in the EU must be lead-free from July 1, 2006.¹⁾ Then, the manufacturing, performance, and reliability criteria for solder joints have become increasingly complex as relationships between the solder alloy, the circuit board materials and construction. Many alloys are being investigated as substrates for Sn-Pb eutectic solder.^{2,3)} In order to develop lead-free soldering technology, considerable research efforts into characteristics of lead-free solder such as the microstructure, mechanical properties and interfacial reactions are in progress.⁴⁻¹⁰⁾ Among various lead-free alloys, Sn-Ag(-Cu) system solders are currently considered the most promising lead-free solders for both wave and reflow soldering technology.

The high reaction rate of metals in molten lead-free solders (the high dissolution rate of metals) was pointed out as the basic characteristic of lead-free solders. For example, Takemoto *et al.*¹¹⁾ showed that the dissolution of iron in molten solder did occur and the dissolution of iron in lead-free solders was greater than that in the conventional Sn-Pb eutectic solder. And they found that the addition of Fe to Sn-3.5Ag solder effectively reduces the dissolution rate of iron. Nishikawa *et al.*¹²⁾ investigated the reaction between Sn-Ag-Cu solder and plated iron to reveal the effect of iron-plating conditions on reactions in molten solder. As a result, it was clear that the dissolution of plated iron into molten lead-free solders was largely attributable to the grain size of the plated surface and the dissolution rate decreased with the increase in the grain size. Then, the effect of the addition of Co to Sn-3.5Ag solder on the dissolution of plated iron was investigated,¹³⁾ rather than the addition of Fe, and the results

clearly showed that the addition of Co to Sn-3.5Ag solder was effective in reducing the dissolution thickness of plated iron. Additionally, a reaction test between Co-added solders and phosphorous-deoxidized copper plate was performed, and it was found that the thickness of intermetallic compound (IMC) formed at the interface between Sn-Ag-Co solder and copper plate drastically increased compared with the case of binary Sn-3.5Ag solder, regardless of Co content in the reflow process. Moreover, to improve the characteristics of lead-free solders, the effect of the addition of minor elements such as Ni, Co, In, Zn, Ge, La, Ce to lead-free solders on the properties of solder and interfacial reactions have been explored in the world.¹⁴⁻²⁰⁾ Chaung *et al.*¹⁷⁾ investigated the IMCs formed during the reflow and aging of Sn-3.0Ag-0.5Cu solder and Sn-3.0Ag-0.5Cu-0.06Ni-0.01Ge solder ball grid array (BGA) packages with Au/Ni surface finishes. They reported that the growth thickness of the interfacial intermetallic layers and the consumption of the Ni surface-finished layer on the Cu pads in Sn-3.0Ag-0.5Cu-0.06Ni-0.01Ge solder joints are both slightly less than those in Sn-3.0Ag-0.5Cu.

The formation of IMCs in solid/liquid reaction couples are primarily controlled by the dissolution processes of base metals. It is well known that the presence of the IMCs between solders and base metals is an indication of good metallurgical joint. However, the IMC thickness of the interface between the solder and substrate is very important for the reliability of the solder joint. The thick IMC layer is generally sensitive to stress and provides sites of initiation and paths of propagation for cracks, since such layer is brittle. From the viewpoint of electronic package reliability, it is significant to understand the relationship between the morphology at the interface and the joint strength. Then, due to the rapid formation of Cu-Sn IMC at the tin-based solder/Cu interface during the soldering process, the reliability of this type of solder joint is a concern.²¹⁾ Therefore the electroless nickel-phosphorous (Ni-P) layer was, in some

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Fig. 1 Schematic diagram of test specimen and bump pull test. (a) Test specimen, (b) Pull test method for solder bump.

instances, deposited on the Cu substrate as a diffusion barrier between Cu and the solder materials.^{22,23)} In this study, the microstructure at the interface and the pull strength of Sn-Ag(-Ni or Co) solder with a Cu pad and with a nickel-phosphorous (Ni-P) metallization was studied in order to clarify the effect of the addition of the minor element, Ni or Co, on the formation of IMC at the interface and the joint strength.

2. Experiments

In this study, binary Sn-3.5 mass%Ag solder was used as the basic solder and Sn-3.5 mass%Ag-0.1 mass%Ni, Sn-3.5 mass%Ag-0.1 mass%Co and Sn-3.5 mass%Ag-0.3 mass%Co were specially prepared as the solder added minor elements. The FR-4 (square 40 mm × 40 mm, 25 pads) was selected as the test board material. Figure 1 shows the schematic diagram of test specimen and bump pull test. The pads of the substrates used in this study comprised two different metallization layers, i.e. bare Cu and electroless Ni-8 mass%P (5 μm)/immersion Au over an underlying Cu pad. The diameter of the pad was 0.8 mm. After the test board was immersed in a 4% HCl solution for 120 s and rinsed with ethanol solution, solders (3.9 mg) treated with activated flux were put on each pad. The test board was then placed in a radiation furnace with a nitrogen atmosphere. In the reflow process, the solder was preheated at 373 K for 120 s and subsequently heated at 523 K for 60 s. The solder bump had a height of approximately 1.1 mm on average. After the reflow process, for aging process, some test samples were heat-treated in an oil bath at 423 K for 168 h, 504 h and 1008 h.

A scanning electron micrograph (SEM) was used to observe the interface between the solder and substrate. All SEM images were obtained using the backscattered electron mode. The thickness of the IMC at the interface was measured using a SEM or an optical microscope. An optical microscope was used to observe the fracture surface after the pull test. An electron probe microanalyzer (EPMA) was used to determine the composition of the IMC. The solder bump was subjected to a pull test using a bump pull tester (Rhesca Co., STR-1000, Japan). The pull speed was fixed at 0.3 mm/s for all samples. The pull strength of each condition was estimated by the average of 15 trials.

3. Results and Discussion

3.1 Formation and growth of IMC at the interface

Figure 2 shows the backscattered electron images of the

Fig. 2 SEM photographs of the interface between the solder and Cu pad just after reflow at 523 K for 60 s.

cross section of the Sn-Ag(-Ni or Co) solder/Cu pad interface obtained after the reflow process at 523 K for 60 s. These pictures show the presence of IMCs at the interface between the solder and a Cu pad. Two types of IMCs can be observed. The morphology of the IMC at the interface of the Sn-Ag-Ni or Co solders was quite different from that for the binary Sn-Ag solder. In the case of the binary Sn-Ag solder, the intermetallic layer in the shape of typical scallop was formed between the solder and Cu pad. This intermetallic was identified to be Cu_6Sn_5 by EPMA analysis. In contrast, at the interface of the ternary Sn-Ag-Ni or Co solders, the IMC layer had coral-like morphology,¹⁵⁾ and some portions of solders were trapped in the IMC layer. By EPMA analysis, it was found that the IMC layer contained Ni or Co element added to the solder, which was enriched especially at the outer region of the IMC layer. The IMC phase was respectively confirmed as $(\text{Cu},\text{Ni})_6\text{Sn}_5$ and $(\text{Cu},\text{Co})_6\text{Sn}_5$. The same tendency concerning IMC formation had been found in the previous study using phosphorous-deoxidized copper plate.¹³⁾ In other recent study,²⁴⁾ the thermodynamic models were applied in order to analyze the influence of additives during the interfacial reaction and the interaction parameters were predicted to evaluate the affinity among the component elements. As a result, the affinities of Sn-Ni and Sn-Co were higher than that of the Sn-Cu couple. That could explain qualitatively why both Ni and Co were involved in the IMCs of Cu_6Sn_5 .

Figure 3 shows the backscattered electron images of the cross section of the Sn-Ag(-Ni or Co) solder/electroless Ni-P plating interface obtained after the reflow process at 523 K for 60 s. As shown in this figure, there is little effect of the Ni or Co addition to the solder on the morphology of the IMC layer at the interface. Regardless of the minor element addition, the complicated thin IMC layer was formed at the interface. In the case of the addition of Co, some particles of IMCs were observed in the solder matrix. By using EPMA,

Fig. 3 SEM photographs of the interface between the solder and Ni-P plating just after reflow at 523 K for 60 s.

Fig. 5 SEM photographs of the interface between the solder and Ni-P plating after aging for 1008 h at 423 K.

Fig. 4 SEM photographs of the interface between the solder and Cu pad after aging for 1008 h at 423 K.

the composition of the IMCs at the interface and in the solder matrix was analyzed. In the cases of Sn-Ag solder and Sn-Ag-Ni solder, it was found that the IMC of Ni_3Sn_4 was formed at the interface. In the case of Sn-Ag-Co solder, the IMC of Ni_3Sn_4 contained a little Co element was formed at the interface. Concerning the IMC particles in the solder matrix, the composition was confirmed as CoSn_2 .

The backscattered electron images of the interface between the Sn-Ag(-Ni or Co) solder and a Cu pad after aging process at 423 K for 1008 h were shown in Fig. 4. The growth of the IMC at the interface of the Sn-Ag-Ni or Co solders was quite different from that for the binary Sn-Ag solder as well as just after reflow process. For the binary Sn-Ag solder, the

morphology of the IMC layer became smooth, and the thick second layer, that was darker phase adjacent to the Cu pad, was clearly observed at the interface. The layer adjacent to the Cu pad was Cu_3Sn . For the Sn-Ag-Ni or Co solders, portions of solder trapped in the IMC layer tended to disappear. The very thin second layer, Cu_3Sn , was found at the interface between the Cu pad and the first layer, Cu_6Sn_5 , and the Cu_3Sn intermetallic layer at the interface of the Sn-Ag-Ni or Co solder grew much more slowly than that of the Sn-Ag solder.

The backscattered electron images of the interface between the Sn-Ag(-Ni or Co) solder and an electroless Ni-P plating after aging process at 423 K for 1008 h were shown in Fig. 5. Compared to the IMC layer just after reflow process shown in Fig. 3, the intermetallic layer at the interface clearly grew and became thick regardless of the solder composition. The effect of the minor element addition to the solder on the growth of the IMC layer was not clear.

Figure 6 shows the total thickness of IMC layers at the interface between the solder and Cu pad as a function of solder composition and the aging time. Just after reflow process, aging time is 0 h, the IMC thicknesses for the Sn-Ag-Ni or Co solder were much thicker than that for the binary Sn-Ag solder. This means that adding Ni or Co to the solder enhances the IMC formation during the reflow process. The IMC thicknesses for the Sn-Ag-Ni or Co solder were almost similar in all the solder added the minor element. According to work by other researches,¹⁵⁾ it has been pointed out that the solidification catalyst effect of Co promotes reduced undercooling and seems to enhance the nucleation site density of the Cu_6Sn_5 . And as mentioned in the previous study,¹³⁾ Co may be an effective nucleation site for the Cu_6Sn_5 phase and the addition of Co to the solder appears to enhance the formation of the IMC phase in the solder. Ni may have a similar effect, too. Hence, IMC containing Ni or Co is deposited on the Cu_6Sn_5 layer, and the IMC thickness for the

Fig. 6 Effect of aging time at 423 K on the total IMC thickness between the solder and Cu pad.

Fig. 7 Effect of aging time at 423 K on the total IMC thickness between the solder and Ni-P plating.

Sn-Ag-Ni or Co solder increased drastically as compared with that of the binary Sn-Ag solder. During aging process at 423 K, total IMC thickness in all solders increased with the increase of the aging time. Especially, the growth rate of the IMC layer for the binary Sn-Ag solder was much greater than that for the Sn-Ag-Ni or Co solder. After aging process for 1008 h, all the solders had similar IMC thickness. Within this test, the addition of Ni or Co to the solder was effective to reduce the growth rate of the IMC layer at the interface with Cu pad during aging process.

Figure 7 shows the total IMC thickness at the interface between the Sn-Ag(-Ni or Co) solder and electroless Ni-P plating just after reflow and after aging process. Just after reflow process, regardless of the Ni, Co addition, all the solders had almost similar IMC thickness, and the thickness was only 1 μm. Even after aging for 1008 h, the IMC thickness was only 3 μm for all the solders. The IMC

thickness at the interface for electroless Ni-P plating was clearly thinner than that for a bare Cu during the aging process. The addition of Ni or Co to the solder was not affected to the growth of IMC layer at the interface with electroless Ni-P plating during aging process.

Therefore, for using a Cu as a metallization layer of the substrate, the addition of Ni or Co was very effective for the IMC formation and growth at the interface during reflow and aging process. On the other hand, for using a electroless Ni-P plating as a metallization layer of the substrate, the IMC formation and growth at the interface was not affected by the Ni or Co addition to the solder. These differences concerning the IMC layer are probably associated with the phase of the IMC formed at the interface and the substitution of Ni or Co for Cu atom in binary compounds with Sn, Cu_6Sn_5 .

3.2 Joint strength of solder bump

In order to evaluate the effect of the morphology of the IMC layer at the interface on the joint strength and the fracture mode of solder bumps, a bump pull test was performed. The pull test is a commonly employed method for estimating the strength of the joint interface. Figure 8 shows the average pull strengths of the Sn-Ag(-Ni or Co) solder joints with a Cu pad and the effect of the aging time on the pull strength of the solder joints. The pull strength in all solders slightly degraded with the increase of the aging time. The addition of Ni or Co to the solder was not affect to the joint strength of the solder joints with a Cu pad, although, as shown in Figs. 2 and 4, the IMC morphology at the interface of the Sn-Ag-Ni or Co was quite different form that for the binary Sn-Ag solder after reflow and aging process. After the bump pull test, fracture surfaces of the solder bump were observed, and the fracture could be clearly classified into two modes, fracture through the solder and fracture along the interface between the solder and pad. Figure 9 shows SEM image of the typical fracture along the interface between the solder and pad for the solder joint using Sn-3.5Ag-0.3Co solder. By EPMA analysis, it was confirmed that the fracture progressed among the interface between the solder and pad. Table 1 shows the ration of fracture along the interface with a

Fig. 8 Effect of aging time at 423 K on the pull strength of the solder/Cu pad joint.

Fig. 9 SEM micrograph of typical fracture along the interface for the solder joint using Sn-Ag-0.3Co solder.

Table 1 Ration of fracture along the interface in 15 trials for each solder bump with a Cu pad.

Aging time (h)	Sn-3.5Ag	Sn-3.5Ag -0.1Ni	Sn-3.5Ag -0.1Co	Sn-3.5Ag -0.3Co
0	0	2/15	6/15	11/15
168	0	9/15	7/15	5/15
504	0	11/15	9/15	3/15
1008	0	14/15	15/15	6/15

Cu pad in 15 trials for each solder composition as a function of the aging time. The fracture mode of the Sn-Ag-Ni or Co solders was clearly different from that for the binary Sn-Ag solder. For the Sn-Ag solder joint, the fracture propagated through the solder in all tests after reflow and aging process. Meanwhile, for the Sn-Ag-Ni or Co solder joints, the fracture for some tests occurred along the interface, and the ration of fracture along the interface basically increased with increasing the aging time. The difference in fracture mode between Sn-Ag solder joint and Sn-Ag-Ni or Co solder joint may be caused by the morphology of the IMC layer at the interface.

Figure 10 shows the average pull strengths of the Sn-Ag(-Ni or Co) solder joints with a electroless Ni-P plating and the effect of the aging time on the pull strength of the solder joints. Just after reflow process, the pull strengths in all solders are almost similar. Then, during aging process, the pull strength of Sn-Ag-Co solder joints clearly degraded with the increase of the aging time and, particularly, the strength decreases considerably at the first stage of the aging period from 0 h to 108 h compared to the Sn-Ag solder and the Sn-Ag-Ni solder. After aging process for 1008 h, the pull strength of the Sn-Ag-Co solder joints was lower than that of the Sn-Ag solder and the Sn-Ag-Ni solder joints. Table 2 shows the ration of fracture along the interface with an electroless Ni-P plating in 15 trials for each solder composition as a function of the aging time. Obviously, the fracture mode was difference between Sn-Ag(-Ni) solders and Sn-Ag-Co solders. In the case of Sn-Ag-Co solder, except one test, fracture propagated through the solder in all tests after reflow and aging process. The ration of fracture along the interface for Sn-Ag-Co solders was much more than that for

Fig. 10 Effect of aging time at 423 K on the pull strength of the solder/Ni-P plating joint.

Table 2 Ration of fracture along the interface in 15 trials for each solder bump with a electroless Ni-P plating.

Aging time (h)	Sn-3.5Ag	Sn-3.5Ag -0.1Ni	Sn-3.5Ag -0.1Co	Sn-3.5Ag -0.3Co
0	8/15	7/15	14/15	15/15
168	0	1/15	15/15	15/15
504	3/15	1/15	15/15	15/15
1008	0	4/15	15/15	15/15

Fig. 11 SEM photographs of the interface between Sn-3.5Ag-0.3Co solder and electroless Ni-P plating using a low magnification.

Sn-Ag(-Ni) solders. To interpret why the solder joint of the Sn-Ag-Co solders, except the Sn-Ag-Ni solder, showed the fracture along the interface, the interface between the Sn-Ag-Co solder and electroless Ni-P plating was observed by using a low magnification SEM. The image at a low magnification was shown in Fig. 11. Many particles of IMC were observed in the solder matrix, and the composition of the IMCs was confirmed as CoSn_2 phase. So in the case of Sn-Ag-Co solder joint with electroless Ni-P plating, IMC particles were formed near the interface. So, the fracture

along the interface may be attributed to the IMC particles near the interface due to the brittle property of the IMC.

Therefore, for using a Cu as a metallization layer of the substrate, the addition of Ni or Co to the solder did not affect the pull strength of the solder bump, but it did affect the fracture mode. On the other hand, for using an electroless Ni-P plating as a metallization layer of the substrate, the addition of Co, except Ni, was effective for the pull strength and the fracture mode during aging process.

4. Conclusions

The microstructure at the interface and the pull strength of Sn-Ag(-Ni or Co) solder bump were investigated to reveal the effect of the addition of Ni or Co to Sn-Ag solder on the interface between the solder and metallization layer. As a metallization layer of the substrate, bare Cu and electroless Ni-P plating were utilized. For using a Cu pad, the addition of Ni or Co was very effective for the IMC formation and growth at the interface during reflow and aging process. In terms of the joint strength with a Cu pad, the addition of Ni or Co to the solder did not affect the pull strength of the solder bump, but it did affect the fracture mode. In contrast, for using electroless Ni-P plating, the IMC formation and growth at the interface was not affected to the Ni or Co addition. And the addition of Co, except Ni, affected the pull strength and the fracture mode during aging process.

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