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Effects of Minor Additions of Zn on Interfacial Reactions of Sn-Ag-Cu and Sn-Cu Solders with Various Cu Substrates during Thermal Aging

MOON GI CHO,[1] SUNG K. KANG,[2] DA-YUAN SHIH,[2] and
HYUCK MO LEE[1,5]

1.—Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Gusung-Dong 373-1, Yusung-Gu, Daejeon 305-701, Republic of Korea. 2.—IBM T.J. Watson Research Center, 1101 Kitchawan Road, Route 134, Yorktown Heights, NY 10598, USA. 5.—e-mail: hmlee@kaist.ac.kr

The effects of Zn additions to Sn-0.7Cu and Sn-3.8Ag-0.7Cu (all in wt.% unless specified otherwise) Pb-free solders on the interfacial reactions with Cu substrates were investigated. The study was focused on the intermetallic compound (IMC) growth, Cu consumption and void formation as a function of thermal aging and solder composition. Four different kinds of Cu substrates (high-purity Cu, oxygen-free Cu, vacuum-sputtered Cu, and electroplated Cu) were prepared to compare their interfacial reaction behaviors with Zn-added solders. Thermal aging was performed at 150°C for up to 1000 h to accelerate the interfacial reactions between solders and Cu substrates. Growth of IMCs (Cu_6Sn_5 and Cu_3Sn) in Zn-added solders was slower than those without Zn additions. The growth of the Cu_3Sn phase, in particular, was drastically reduced in the Zn-added solders on all four Cu substrates. On an electroplated Cu substrate, numerous voids were observed in the Cu_3Sn phase for Sn-Cu and Sn-Ag-Cu solders aged at 150°C for 1000 h. However, these voids were largely eliminated in the Zn-added solders. On the other three Cu substrates, the conditions which produce a high density of voids were not found after aging both solders with and without Zn. The Cu consumption with Zn-added solders was also significantly lower. The beneficial effects of Zn additions on interfacial reaction behaviors are reported, and the corresponding mechanisms in suppressing void formation and Cu consumption due to Zn additions will be discussed.

Key words: Zn addition, interfacial reaction, intermetallic compounds, void suppression, Cu consumption, thermal aging

INTRODUCTION

Legislation has come into effect, which was passed by the European Union in 2002, to ban the use of Pb and other toxic materials in electronic packaging. The extensive searches for Pb-free solder alloys in the last several years were conducted.[1–4] A few promising Pb-free candidates have been identified for producing reliable Pb-free solder joints, which include Sn-0.7Cu, Sn-3.5Ag-0.7Cu and Sn-3.5Ag-4.8Bi (in wt.% unless specified otherwise). Recently among the Pb-free candidates, the near-ternary Sn-Ag-Cu (SAC) solder alloys have been recognized as the most promising candidates for surface-mounted card assembly, such as BGA (ball grid array) solder joints.[1,2] However, the exact compositions of the near-ternary SAC solder alloys are still in dispute depending on their applications.

Many problems in using the SAC solder alloys have been reported, such as the formation of large

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intermetallic compounds (IMCs), void formation at the interface of a Cu substrate[5,6] and the large undercooling in solidification.[7,8] Recently, many studies have been conducted to solve the problems as well as accomplish more stable and reliable solder joints by adding fourth alloying elements to SAC solder alloys, such as Ni,[9] Ti,[9] Mn,[9] Co,[9,14] Bi,[10] Sb,[11] Zn,[12–14] Fe,[14] and In-Ni.[14] Kim et al. reported that when 0.1 wt.% X (X = Ni, Ti, Mn and Co) was added to Sn-3.0Ag-0.5Cu solder alloys, the fourth alloying elements improved the microstructure and reduced the undercooling, recommending the SAC-0.1Ni solder alloy as an optimum composition.[9] Rizvi et al. reported that when 0.1 wt.% Bi was added to Sn-2.8Ag-0.5Cu solder alloys, it was effective in reducing the growth of Cu-Sn IMCs and the consumption of Cu UBM in the interfacial reaction with Cu UBM.[10] Li et al. found that when Sb was added to Sn-3.5Ag-0.7Cu up to 2 wt.%. IMCs growth on Cu UBM was reduced as the Sb content increased.[11] Kang et al. reported that when 0.1 wt.% and 0.7 wt.% Zn were added to Sn-3.8Ag-0.7Cu, the undercooling dramatically decreased from 29.8°C to 3–4°C and, as a result, the formation of large Ag_3Sn plates was controlled. In addition, they observed that the Zn addition (0.7 wt.%) also affected the suppression of IMCs growth on Cu pads.[12,13] I. De Sousa et al. reported that Zn addition among other alloying elements (Zn, Co, Fe and In-Ni) added to Sn-3.0Ag-0.5Cu solder alloys had the most beneficial effects on IMCs growth, the consumption of Cu UBM and void formation.[14] Although the beneficial effects of the Zn addition to SAC alloys on various interfacial reactions in Sn-rich solders are well documented, the mechanisms of the beneficial effects of Zn addition are not clearly understood yet. Furthermore, since Zn has an adverse effect on the wettability of SAC solder joints,[15] it is important to find an optimum level of Zn addition. The purpose of the present work is to investigate the effects of minor Zn alloying addition on the interfacial reaction of Sn-0.7Cu and Sn-3.8Ag-0.7Cu on various Cu substrates during thermal aging. The interfacial reactions are compared with one another, focused on the IMCs growth, Cu consumption and voids formation. Accordingly four different types of Cu substrates are used in this study: high-purity Cu (HPC), oxygen-free Cu (OFC), vacuum-sputtered Cu (SPC) and electroplated Cu (EPC). HPC, OFC and EPC are for the observation of IMCs growth and voids formation as well as for the investigation of the Cu substrate effect on the interfacial reactions. SPC is for the observation of Cu consumption. Finally, the mechanisms of the beneficial effects of Zn addition to SAC alloys are discussed based on the experimental findings and thermodynamic calculations.

EXPERIMENTAL PROCEDURE

The basic solder compositions used in this experiment are Sn-0.7Cu and Sn-3.8Ag-0.7Cu. Two Zn-added solder alloys were commercially produced for the nominal compositions of Sn-0.7Cu-0.4Zn and Sn-3.8Ag-0.7Cu-0.4Zn. Four different types of Cu substrates (HPC (99.9999%), OFC (99.99%), SPC, EPC) were employed as the purity of Cu substrates and materials processing methods. The substrate size used was 6 mm × 6 mm for all interfacial reactions study. The approximately same solder weight (70 mg) was used to eliminate any effects due to the variation in solder volume. The interfacial reaction experiment was conducted by reflowing the same amount of a solder on a Cu substrate on a hotplate at 260°C for 2 min. Subsequently, an aging experiment was conducted in a nitrogen oven at 150°C up to 1000 h.

In another experiment, two other Zn-added solders were commercially produced with the nominal compositions of Sn-3.8Ag-0.7Cu-0.1Zn and Sn-3.8Ag-0.7Cu-0.7Zn. The interfacial reaction experiments conducted by using only electroplated Cu substrate. The same conditions for the interfacial reactions and aging were used: reflow for 2 min at 260°C, aging for 500 h and 1000 h at 150°C.

After reflow and aging, the interface of solders and Cu substrates was revealed on its cross section by mounting and polishing. Each interface was etched by the solution of 92% methanol, 5% nitric acid and 3% hydrochloric acid. Optical microscopy and scanning electron microscopy (SEM) were employed to characterize the IMCs. The back-scattered electron mode of SEM was used to observe the IMCs, and energy-dispersive X-ray spectroscopy (EDS) and electron probe micro-analyzer (EPMA) for compositional analyses. Moreover, a focus ion beam (FIB) technique was also used to study the fine details of the interface.

Furthermore, thermodynamic calculations were performed to explain the experimental results, by using the Thermo-Calc thermodynamic software developed at the Royal Institute of Technology, Stockholm, Sweden.[16]

RESULTS

IMC Growth During Thermal Aging at 150°C

Figure 1 is the collection of all cross-sectional images of four different solders and three different Cu substrates after the reflow and aging for 1000 h at 150°C. The first row exhibits the SEM images of the representative interface between four solders (Sn-0.7Cu:SC, Sn-0.7Cu-0.4Zn:SCZ, Sn-3.8Ag-0.7Cu:SAC and Sn-3.8Ag-0.7Cu-0.4Zn:SACZ) and a Cu substrate (high-purity Cu) after the reflow. The second, third and fourth rows exhibit the cross-section SEM images on high-purity Cu (HPC), oxygen-free Cu (OFC), and electroplated Cu (EPC), respectively, after aging for 1000 h at 150°C. The scallop-like Cu_6Sn_5 IMCs were observed commonly at the interface of all solders, and partially Cu_3Sn IMCs were found after the reflow. When the aging was conducted up to 1000 h, the total IMC thickness

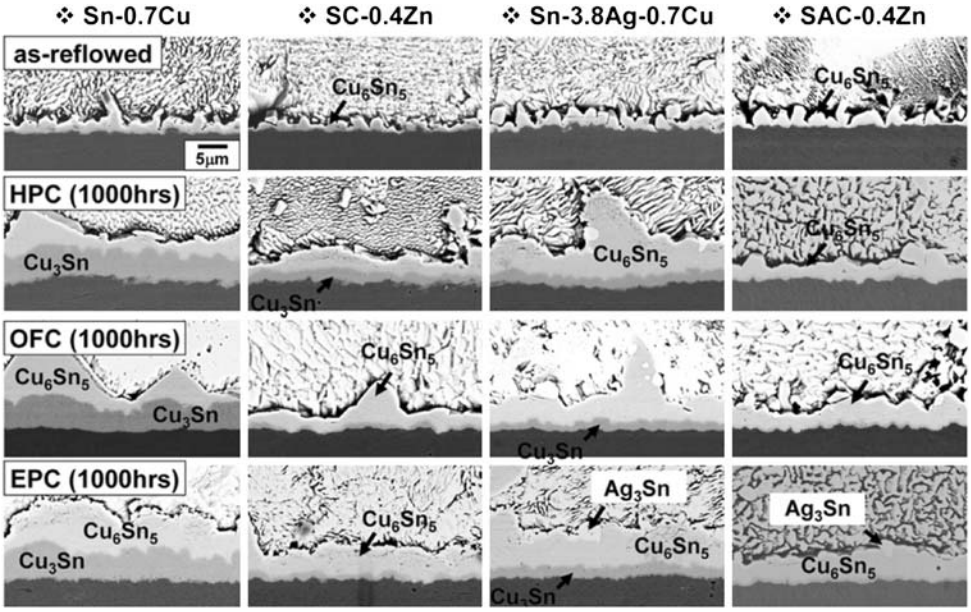

Fig. 1. The cross-sectional images of Sn-0.7Cu, Sn-0.7Cu-0.4Zn, Sn-3.8Ag-0.7Cu and Sn3.8Ag-0.7Cu-0.4Zn solders on high-purity Cu, oxygen-free Cu and electroplated Cu after the reflow and aging for 1000 h at 150°C.

in all solders became thicker than in as-reflowed, and Cu_3Sn IMCs were observed at the entire interface of all solders. In addition the morphology of Cu_6Sn_5 changed to a layer shape. The general interfacial reaction behavior of four solders was not much different. However, in terms of IMC growth, there was a big difference between Zn-added solders and non Zn-added solders after the aging. The IMC thickness of Zn-added solders (SC-0.4Zn and SAC-0.4Zn) was much thinner than with SC and SAC as shown in Fig. 1. The thickness of each IMC in Fig. 1 was measured by the image analysis software program and compared the growth of each IMC as a function of solders and Cu substrates in Fig. 2. The thickness of Cu_6Sn_5 and Cu_3Sn as well as total IMCs was reduced by adding 0.4 wt.% Zn to SC and SAC. The reduction of Cu_3Sn growth between SC solder and SC-0.4Zn solder was distinguished. Meanwhile, the growth of Cu_3Sn in SAC solder was not as much as that in SC solder. Accordingly, the Zn addition was more effective in SC than in SAC in suppressing the Cu_3Sn IMCs growth.

On the other hands, the similar trend of the Zn effect on IMCs growth was observed with all three different Cu substrates (HPC, OFC and EPC). However, comparing the IMCs thickness of each solder on three different Cu substrate, the thickness of total IMCs as well as Cu_6Sn_5 on HPC and OFC was a little thinner than on EPC.

Cu Consumption During Thermal Aging at 150°C

Figure 3 is a collection of the cross-section images of four solders on sputtered Cu (SPC) for the conditions of as-reflowed, and thermally aged for 125 h and 250 h. Differently from the previous other Cu substrates (HPC, OFC and EPC), a relatively short aging treatment with the SPC samples was conducted to demonstrate the early stage of Cu consumption and IMCs formation. The initial thickness of SPC was 4 μm. The progression of Cu consumption and IMCs formation can be clearly followed with all four different solder joints in Fig. 3 (SC, SCZ, SAC and SACZ). In Fig. 3, after the aging, Cu_6Sn_5 and Cu_3Sn were observed at the interface of all four solders. The IMC thickness of Zn-added solders (SC-0.4Zn and SAC-0.4Zn) was thinner than that of SC and SAC, more significantly in SCZ than in SACZ. The growth of Cu_3Sn was largely reduced by the Zn addition. Commonly, the IMCs growth and Cu consumption are proportional to each other because Cu atoms of the substrate (or UBM) participate in the interfacial reaction with Sn atoms of solder alloys, and then Cu_6Sn_5 and Cu_3Sn are formed at the interface of solders and Cu substrates. The thickness of the residual Cu layer underneath the IMC layers was measured by the image analysis software program for each solder and plotted as a function of aging time in Fig. 4. The sputtered Cu layer of 4 μm was all consumed in SC after 250 h, and mostly consumed in SAC after 250 h. However, in the Zn-added solders (SCZ and SACZ), only less than 2 μm sputtered Cu was consumed. The Cu consumption in the as-reflowed condition was less with the Zn-added solders compared to the basic solders and the trend continued during the aging.

Void Formation

When four solders (SC, SC-0.4Zn, SAC and SAC-0.4Zn) were aged up to 1000 h on OFC and HPC, no

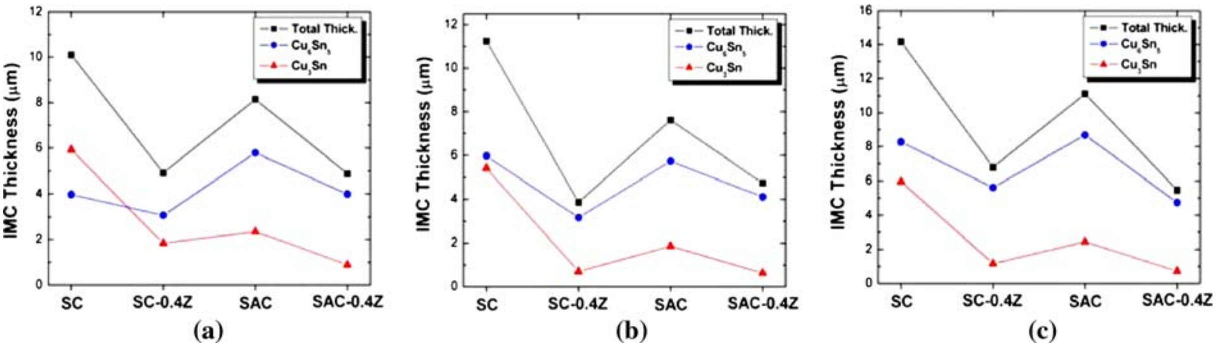

Fig. 2. IMC thickness for each solder after aging for 1000 h at 150°C on (a) high-purity Cu, (b) oxygen-free Cu and (c) electroplated Cu.

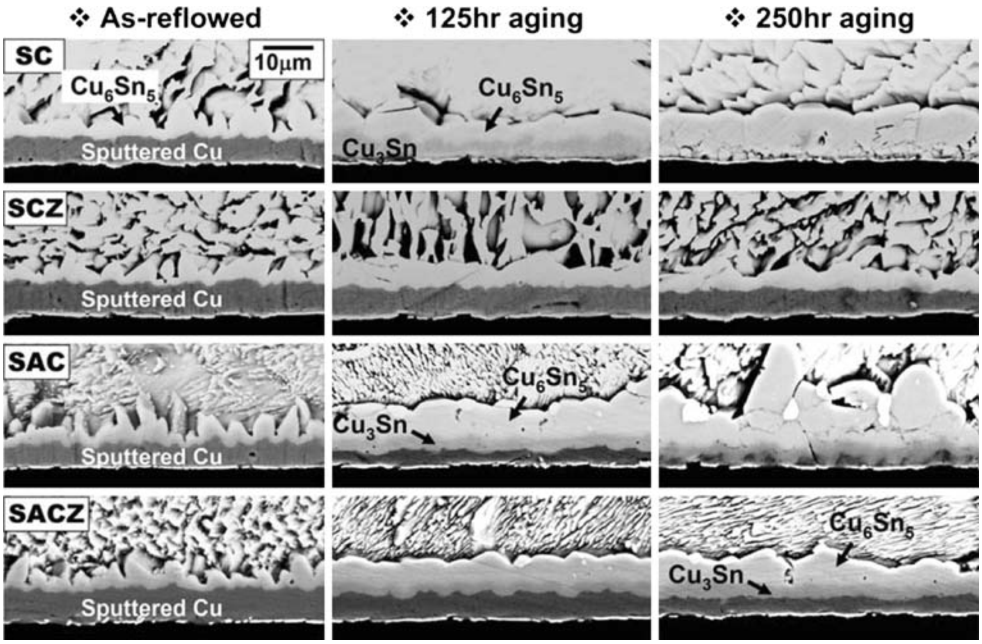

Fig. 3. The cross-sectional images of Sn-0.7Cu, Sn-0.7Cu-0.4Zn, Sn-3.8Ag-0.7Cu and Sn-3.8Ag-0.7Cu-0.4Zn solders on sputtered Cu after the reflow and aging for 125 h and 250 h at 150°C.

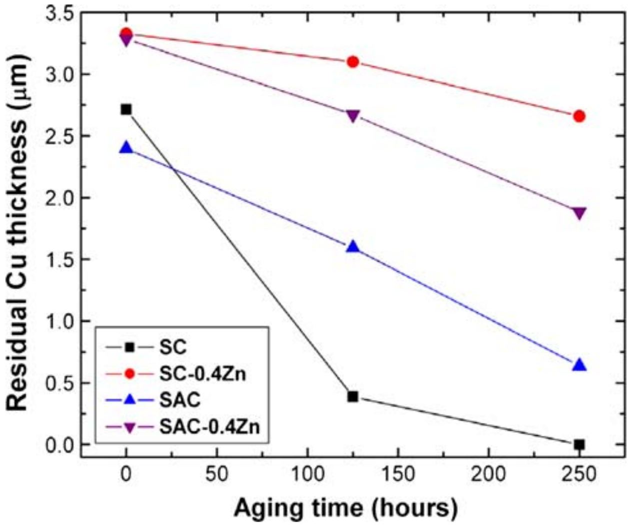

Fig. 4. The residual Cu thickness of each solder on sputtered Cu, which was plotted as a function of aging time.

voids were observed at the interface, as shown in Fig. 1. Therefore, no beneficial effect of Zn addition on void formation was noted on OFC and HPC. However, on electroplated Cu a few voids were found in the case of SC and SAC, while no voids were observed in SC-0.4Zn and SAC-0.4Zn, as shown in Fig. 1. In order to further investigate the void formation on the electroplated Cu, the interface area of each sample was cut out by using the FIB technique. Figure 5 is a collection of secondary electron images of the FIB samples, showing the interface between each solder and the electroplated Cu after aging for 1000 h at 150°C. Several voids were found at the interface of SC and SAC on EPC, while no voids at the interface of SC-0.4Zn and SAC-0.4Zn were found. Therefore, although voids were not always formed at the interface of SC and SAC on all Cu substrates, 0.4 wt.% Zn addition to SC and SAC suppressed the void formation on a special Cu substrate such as the electroplated Cu used in this study.

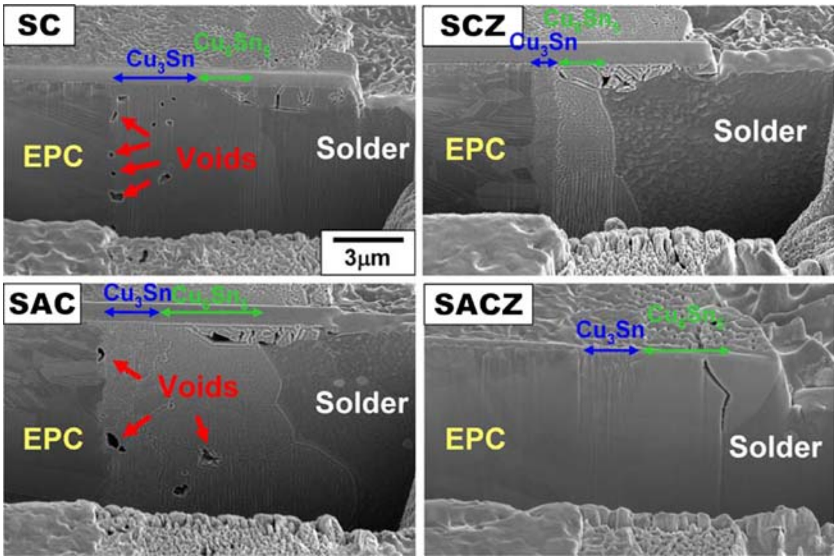

Fig. 5. Secondary electron images of the interfacial area between each solder and electroplated Cu after aging for 1000 h at 150°C, which was cut out by the focused ion-beam (FIB) technique.

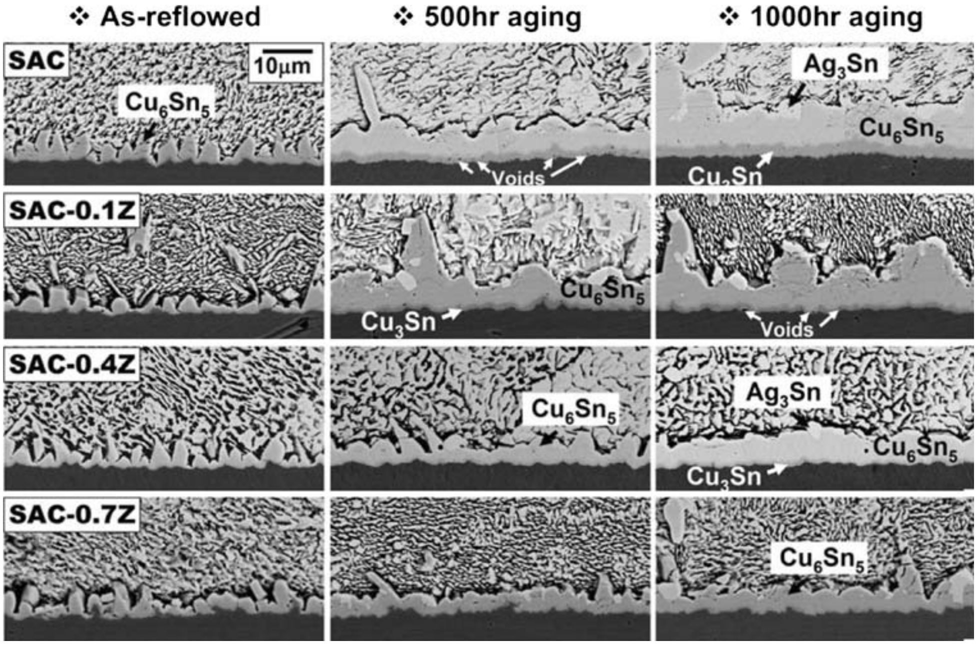

Fig. 6. The cross-section images of Sn-3.8Ag-0.7Cu, Sn-3.8Ag-0.7Cu-0.1Zn, Sn-3.8Ag-0.7Cu-0.4Zn and Sn-3.8Ag-0.7Cu-0.7Zn solders on electroplated Cu after the reflow and aging for 500 h and 1000 h at 150°C.

Effective Zn Composition

In order to define an optimum range of minor Zn content, two more commercially produced Zn-added SAC alloys were obtained; Sn-3.8Ag-0.7Cu-0.1Zn and Sn-3.8Ag-0.7Cu-0.7Zn. Figure 6 is a collection of the cross-section images of SAC-XZn (X = 0, 0.1, 0.4 and 0.7 wt.%) reflowed on EPC and aged for 500 h and 1000 h. The identity of IMCs formed at the interface of each solder was not different from the Zn content changes from 0.1 wt.% to 0.7 wt.% in SAC solder. Cu_6Sn_5 IMCs as well as partially Cu_3Sn IMCs were formed for all Zn contents in the reflowed conditions. Then after the aging, Cu_6Sn_5 and Cu_3Sn were found. However, the thickness of each IMC varied depending on the Zn content. The thickness of each IMC layer was plotted as a function of Zn composition in SAC, as shown in Fig. 7. In general, the thickness of each IMC decreased as the Zn content increases. All IMCs of SAC-0.7Zn were much thinner than those of SAC-0.4Zn. Especially,

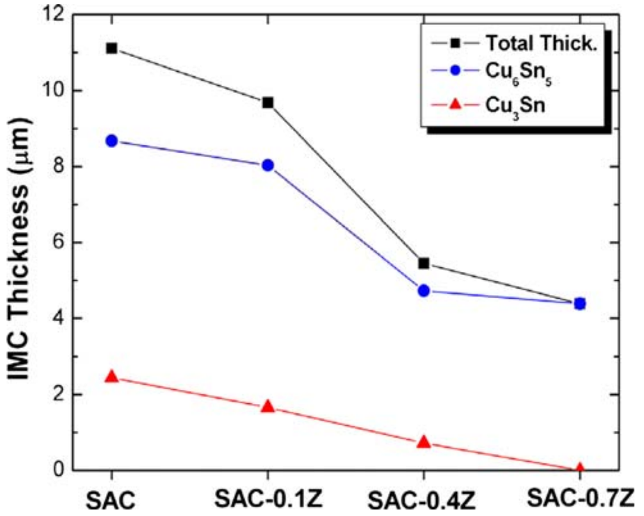

Fig. 7. The thickness of each IMC layer plotted as a function of Zn composition in SAC after aging for 1000 h at 150°C on electroplated Cu.

Cu_3Sn was almost not formed in SAC-0.7Zn even after aging for 1000 h. However, all IMCs of SAC-0.1Zn were much thicker than those of SAC-0.4Zn, but not significantly different from the SAC without Zn. Hence, the 0.4 wt.% Zn addition was much more effective than the 0.1 wt.% Zn in terms of the reduction of IMCs growth in SAC.

The void formation at the interface of SAC-0.1Zn and SAC-0.7Zn on EPC was investigated. Voids were almost never observed in SAC-0.7Zn and SAC-0.4Zn, while a few voids were found in the Cu_3Sn IMCs of SAC-0.1Zn. It seems that void formation was not suppressed by 0.1 wt.% Zn addition.

Based on the present investigation, the Zn addition to SAC more than 0.4 wt.% is desirable to obtain the full beneficial effects (the reduction of IMC growth and suppression of void formation). Considering a possible wettability issue of Zn containing solder,[15] it is also recommended to keep the Zn addition as low as possible.

DISCUSSION

The interface structure and chemistry of SC-0.4Zn and SAC-0.4Zn were investigated in depth to understand the mechanisms of the beneficial effects of Zn addition. First the distribution of all elements (Sn, Cu and Zn) near the interface was identified by line scan of EPMA. As shown in Fig. 8, the distribution of Cu and Sn was analyzed to identify each layer such as Cu substrate, Cu_3Sn, Cu_6Sn_5 and solder near the interface. Zn atoms were detected in addition to Cu and Sn atoms at the interface between Cu and Cu_3Sn. Considering that the source of Zn was the solder inside and the composition was only 0.4 wt.%, this result was very interesting. By the way a similar observation with ours was previously reported by Kang et al.[13] In their works, the interfacial reaction was the liquid-state reaction between molten solders of 0.7 wt.% Zn and Cu pads during reflow. They proposed that the accumulation of Zn atoms at the interface contributed to the reduction of IMCs growth as a diffusion barrier of Cu atoms during reflow. In the present study, a positive identification of the Zn accumulated layer was pursed to present a more concrete mechanism on the beneficial effects of Zn addition. The Zn accumulation layer could be Cu-Zn IMCs or Cu-Zn alloys (solid solution). By FIB and high resolution SEM study, no other IMCs except Cu_6Sn_5 and Cu_3Sn was not found at the interface area, as shown in Fig. 9. Then, the Zn accumulation layer might be a layer of Cu-Zn solid-solution alloys, considering that the solubility of Zn in Cu reaches up to ~35 wt.% at 150°C.[17] Additional information obtained from an etching experiment may provide some clue on this question. The interface area of various Zn-added solders was etched with a solution of NH_4OH and H_2O_2 (3%) in DI water, which is a common etchant used for Cu-Zn alloys.[18] Figure 10 is the SEM images after etching the interface of as-reflowed and aged SAC-0.4Zn and aged SAC on HPC. The interfaces of as-reflowed SAC-0.4Zn and

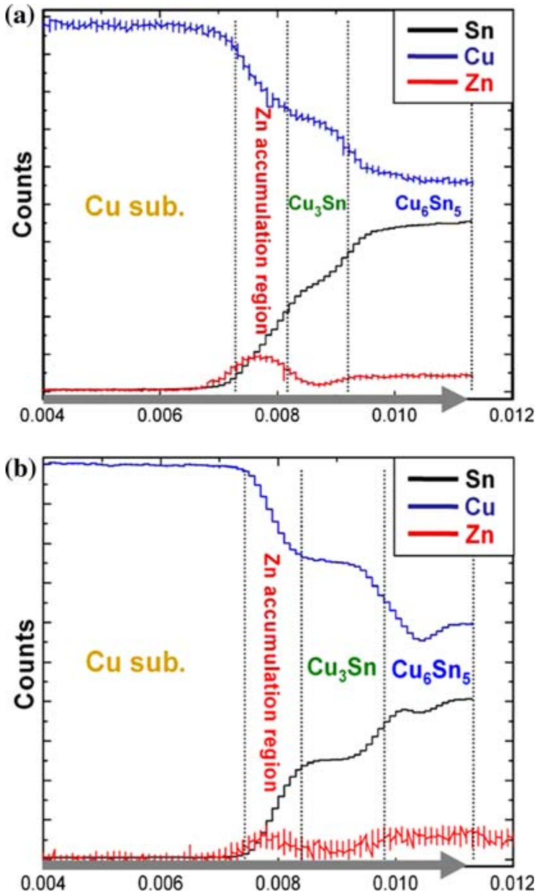

Fig. 8. Compositional profiles of Sn, Cu and Zn are plotted along the distance perpendicular to the IMC interface of (a) Sn-0.7Cu-0.4Zn and (b) Sn-3.8Ag-0.7Cu-0.4Zn.

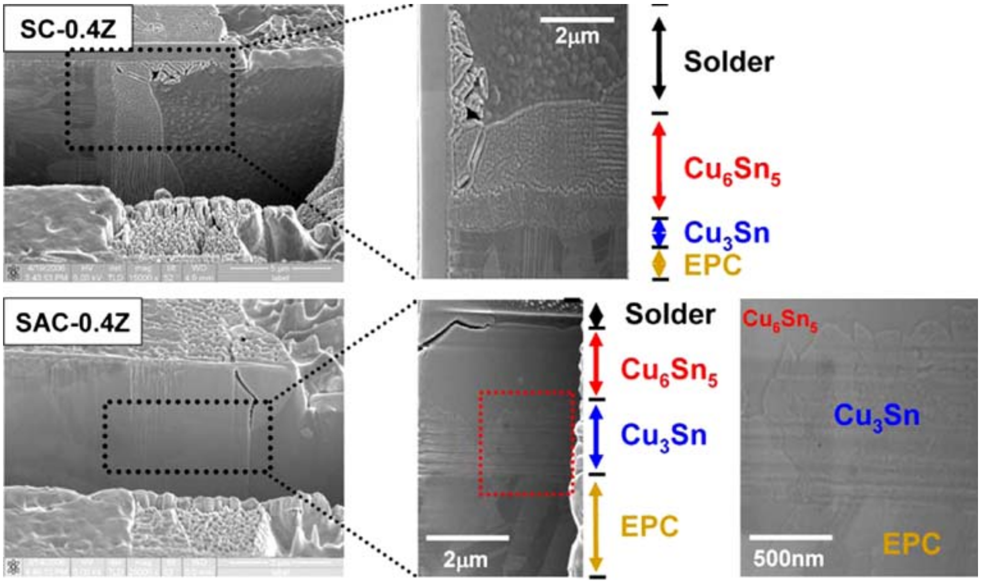

Fig. 9. Higher magnified secondary electron images of the interface between Zn-added solders (Sn-0.7Cu-0.4Zn and Sn-3.8Ag-0.7Cu-0.4Zn) and electroplated Cu after aging for 1000 h at 150°C.

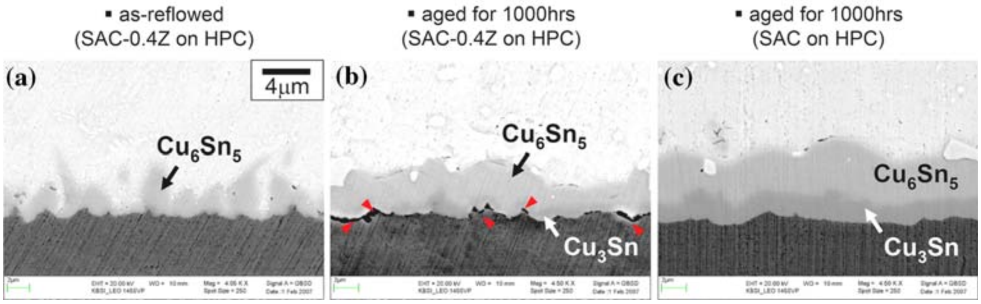

Fig. 10. The back-scatted electron images of the interface on high-purity Cu that was etched by the solution of NH_4OH and H_2O_2 (3%) in DI water; (a) Sn-3.8Ag-0.7Cu-0.4Zn as-reflowed, (b) Sn-3.8Ag-0.7Cu-0.4Zn aged for 1000 h and (c) Sn-3.8Ag-0.7Cu aged for 1000 h.

aged SAC were not attacked by the etchant, and very clean. However, the interface of aged SAC-0.4Zn was attacked partially and the position was between Cu and Cu_3Sn, which matched with the location of the Zn accumulation layer. Therefore, it is claimed that the Zn accumulation layer be a Cu-Zn solid-solution alloy rather than a Cu-Zn IMC layer. Note this deduction is based on an assumption that the etchant used is capable to etch the Cu-Zn solid-solution, but not effective with Cu-Zn IMCs. In addition, it was confirmed from our early observation that the etchant is not effective with Cu-Zn IMCs.

To further develop the above discussion related with the identity of the Zn accumulation layer (Cu-Zn solid-solution alloy), a thermodynamic calculation was performed for the driving force in forming the Cu_3Sn phase in the interface.

Cu_3Sn IMCs can be formed by the reaction between Cu and Cu_6Sn_5, as follows:[19,20]

$$Cu_6Sn_5 + 9Cu\ (FCC) = 5Cu_3Sn \qquad (1)$$

If Cu-XZn alloys instead of a Cu substrate are employed to the reactions, the Eq. 1 can be modified as follows;

$$Cu_6Sn_5 + 9Cu\ (FCC,Cu\text{-}XZn) = 5Cu_3Sn \qquad (2)$$

Cu_3Sn IMCs formed by these equations are dependent on a driving force of their formation. The larger driving force accelerates the more Cu_3Sn IMCs formation. The change of the driving force of Cu_3Sn IMCs formation was calculated by assuming Cu-XZn alloys being participated in the reaction. Basically the driving force of Eq. 1 could be calculated thermodynamically by the Thermo-Calc with the data base of a Sn-Cu binary phase diagram[21] and that of Eq. 2 could be done with the data base of a Sn-Cu-Zn ternary phase diagram.[22] Figure 11 is the result of the thermodynamic calculation for the driving force of Cu_3Sn IMCs formation for the Zn composition up to 30 wt.%. The driving force was 0.968 J/mol in the reaction between pure Cu and Cu_6Sn_5. Interestingly, the driving force decreased

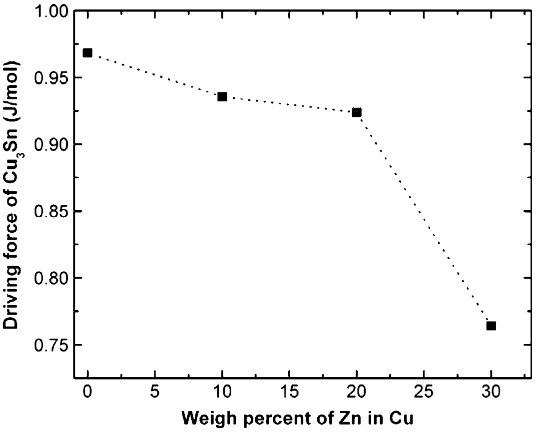

Fig. 11. The driving force of Cu_3Sn IMCs on a Cu-XZn alloy for the Zn composition in Cu up to 30 wt.%, which was calculated by the Thermo-Calc.

as the composition of Zn in Cu increased. It means that as pure Cu changes to Cu-XZn alloy, the diffusion of Cu is retarded, and then the formation of Cu_3Sn IMCs is retarded. The reason is that the activity of Cu in Cu-Zn alloy is lower than in pure Cu. Moreover the effect of Zn addition on the reduction of IMCs growth can be explained by the thermodynamic calculation shown in Fig. 11. This also seems to explain why more Zn addition in SC or SAC solders is more effective in retarding the IMCs growth.

In recent reports, voids that formed at the interface between Cu and IMCs caused serious reliability concerns under impact loading conditions.[5,6,23,24] Besides, the void layer can reduce the joint strength of Pb-free solder joints.[5,23,24] Cu pad or UBM used in most of reports for the voids formation of the Pb-free solder joints was an electroplated Cu. In this study voids was formed on EPC, while not on HPC and OFC (high pure and wrought Cu). It means that the voids formation by the interfacial reaction between Cu and Pb-free solders was dependent on the type of Cu substrate. This result was also consistent with the previous report that when using high pure and wrought Cu, voids formation has been minimized during thermal aging.[24] Nevertheless, in this study, void formation at the interface of SC and SAC on EPC was suppressed by 0.4 wt.% Zn addition. Hence, an improvement of the solder joints' reliability by small Zn addition to SC and SAC is expected. Considering that the void formation over the Cu substrate would be related with the growth of Cu_3Sn IMCs.[5,24,25] Our findings seem self-consistent in terms of IMC reduction and void suppression in Zn-added solders.

Another possible mechanism on the suppression of void formation due to Zn addition is a direct diffusion of Zn to the interface through Cu_6Sn_5 and Cu_3Sn IMCs to fill up any vacancy sites before they grow into a large size of voids. However, to answer this question, further investigations for the relation between Zn addition and void formation are needed in future.

SUMMARY

The effects of minor Zn alloying (0.1–0.7 wt.%) additions on the interfacial reactions of Sn-0.7Cu and Sn-3.8Ag-0.7Cu with various Cu substrates (high-purity Cu, oxygen-free Cu, electroplated Cu and sputtered Cu) were investigated during thermal aging.

The 0.4 wt.% Zn addition was effectivein reducing IMCs' growth (especially Cu_3Sn IMCs) and Cu consumption. In addition, void formation at the interfaces of SC and SAC on a special Cu substrate (electroplated Cu) was dramatically suppressed by 0.4 wt.% Zn addition.

Finally, a mechanism for beneficial effects of Zn additions on the reduction of IMCs' growth and Cu consumption was discussed. The accumulation of Zn atoms at the Cu_3Sn and Cu interface of Zn-added solders was found, and then it was attributed to a layer of Cu-XZn alloy. From thermodynamic calculations, the driving force of Cu_3Sn IMCs formed on Cu-XZn alloy was lower than on pure Cu. Therefore, the reduction of IMCs growth by Zn addition was attributed to the reduction in the driving force for formation of Cu_3Sn IMCs as the Cu interface layer changed to a Cu-XZn solid-solution alloy.

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