Mechanisms for Interfacial Reactions between Liquid Sn-3.5Ag Solders and Cu Substrates

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Intermetallic compounds formed during the soldering reactions between Sn-3.5Ag and Cu at temperatures ranging from 250°C to 375°C are investigated. The results indicate that scallop-shaped η-$Cu_6(Sn_{0.933}\ Ag_{0.007})_5$ intermetallics grow from the Sn-3.5Ag/Cu interface toward the solder matrix accompanied by Cu dissolution. Following prolonged or higher temperature reactions, ε-$Cu_3(Sn_{0.996}\ Ag_{0.004})$ intermetallic layers appear behind the $Cu_6(Sn_{0.933}\ Ag_{0.007})_5$ scallops. The growth of these interfacial intermetallics is governed by a kinetic relation: $\Delta X = t^n$, where the n values for η and ε intermetallics are 0.75 and 0.96, respectively. The mechanisms for such nonparabolic growth of interfacial intermetallics during the liquid/solid reactions between Sn-3.5Ag solders and Cu substrates are probed.

Key words: Sn-3.5Ag/Cu, soldering reactions, intermetallic compounds, nonparabolic growth kinetics

INTRODUCTION

Copper is widely used in a sputtering target assembly as the material for backing plates. Upon the depletion of the target material, the Cu backing plate is debonded from the used target and recycled by being soldered with a new one. Out of environmental concerns, Sn-3.5Ag has been regarded as a promising Pb-free solder because of the merits of high strength, good creep resistance, improved thermal fatigue life, low cost, and ideal wettability with Cu substrates.[1] During the soldering reaction, intermetallic compounds are known to form at the interfaces, thereby attaining the bonding effect between the target material and solder. However, an overgrowth of interfacial intermetallics can induce cracking in the rebonded target assembly.[2] Thus, vital information may be obtained for such an application through the identification of intermetallic phases and analysis of their growth kinetics during the interfacial reactions between the liquid Sn-3.5Ag solders and Cu backing plates.

The solid/solid reactions of Sn-3.5Ag and other Sn-based solders with Cu substrates, which result in the formation of scallop-shaped Cu_6Sn_5 intermetallic compounds at the interfaces, have been investigated extensively.[3–7] As noted by these reports, the intermetallic growths are diffusion-controlled and governed by a parabolic kinetic relation. However, studies on liquid/solid reactions for the related soldering systems over a wide temperature range are scarce, while opinions on mechanisms for the intermetallic growths in this case are varied.[8–15] In this present study, the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates take place at temperatures ranging from 250°C to 375°C for 10–75 min. After the reaction, the morphology and chemical compositions of the intermetallic compounds are probed and identified. The kinetics of intermetallic growth at the interfaces is analyzed through measurement of the intermetallic layer thickness at various reaction temperatures for various times, whereby the mechanisms for the formation of intermetallics at the Sn-3.5Ag/Cu interface during the soldering reaction are investigated.

EXPERIMENTAL

The Sn-3.5Ag (wt.%) solder was prepared by having pure Sn (99.9%) and Ag (99.95%) encapsulated in a quartz tube under a vacuum of 10^{-5} torr and melted at 600°C. The ingot was homogenized at 100°C for 50 h and then rolled into 0.5-mm foil. Copper substrates with dimensions 8 mm × 12 mm were

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cut from a 1-mm Cu plate (99.9% purity), ground with SiC paper, and polished with 1-μm and 0.3-μm Al_2O_3 powders. For the study of interfacial reactions, the Sn-3.5Ag foils were placed on Cu substrates that had been dipped in a rosin mildly activated-type flux. The Sn-3.5Ag/Cu couples were then heated in an infrared furnace under a vacuum of 10^{-3} torr. Soldering reactions were carried out at temperatures between 250°C and 375°C for various times. After reaction, the specimens were cooled to room temperature in 2 min via a water-cooling system installed within the furnace.

The soldered specimens were then cross-sectioned, ground, and polished. The morphology of intermetallic compounds formed in the solder and at the Sn-3.5Ag/Cu interface was observed by scanning electron microscopy (SEM). The chemical compositions were identified using energy dispersive x-ray spectroscopy (EDX). To clarify the mechanism of intermetallic formation during the liquid/solid interfacial reaction, a formerly developed marking technique was adopted:[16] the surface of the solid substrate was partially sputter-coated with a Ta thin film (approximately 1,000 Å in thickness). Because the Ta thin film does not react with the Sn-3.5Ag liquid solder and the Cu substrate, it acted as a reaction marker to identify the original Sn-3.5Ag/Cu interface. For kinetics analysis, the maximum migration distance of reaction front for each intermetallic scallop was measured. The average value of a minimum of 30 measurements for each soldering condition (per reaction temperature and time) was determined to signify the intermetallic thickness (ΔX). By applying this method, any error in measurement caused by the stripping of certain intermetallic scallops away from the interface could be mitigated.

RESULTS AND DISCUSSION

The microstructure of the as-cast Sn-3.5Ag solder is shown in Fig. 1; it contains many fine particles embedded in the Sn-rich matrix. The chemical composition (at.%) of these fine particles is identified as Ag:Sn = 74.3:25.7, which corresponds to the Ag_3Sn phase. The formation of such Ag_3Sn precipitates causes the composition (wt.%) of the matrix to deviate from Sn-3.5Ag to Sn-0.6Ag. Differential scanning calorimetry (DSC) analyses (Fig. 2) reconfirm the eutectic composition of this solder, which possesses a melting temperature of 220°C.

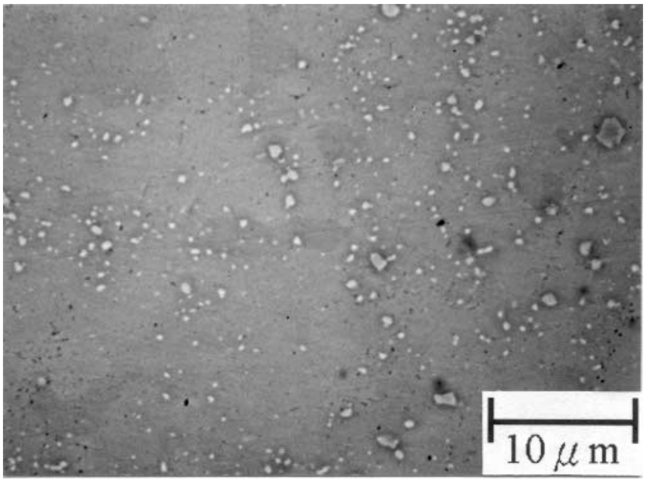

Fig. 1. Microstructure of the as-cast Sn-3.5Ag solder containing fine Ag_3Sn precipitates embedded in the Sn-0.6Ag matrix.

Figure 3 shows the morphology of the intermetallic compounds formed at the Sn-3.5Ag/Cu interfaces after soldering reactions at 250°C for various times; the intermetallics appear in scallop shape and grow with an increase of time into the Sn-3.5Ag solder. The EDX analyses (Table I) indicate that the composition (at.%) of these scallop-shaped intermetallics is Cu:Sn:Ag = 54.40:45.39:0.31, which corresponds to the η-$Cu_6(Sn_{0.993}Ag_{0.007})_5$ phase. Following prolonged soldering reactions, a thin layer of intermetallic compound appears at the $Cu_6(Sn_{0.993}Ag_{0.007})_5$/Cu interface. The composition (at.%, given also by Table I) of these thin intermetallics is Cu:Sn:Ag = 75.21:24.70:0.09, which corresponds to the ε-$Cu_3(Sn_{0.996}Ag_{0.004})$ phase. Along with the formation of η and ε phases at the interfaces, a large number of fine Ag_3Sn particles precipitated in the solder matrix. The composition of the solder matrix as analyzed is Sn:Ag:Cu = 98.30:1.59:0.11 (wt.%) or 97.96:1.83:0.21 (at.%).

As the soldering temperature is increased to 300°C, the interfacial η and ε intermetallics grow more rapidly (Fig. 4). However, the compositions of both intermetallic phases are similar to those soldered at 250°C, as listed in Table I. Figure 4 also indicates that this higher temperature caused the number of Ag_3Sn particles to rise. It has been shown that Cu can dissolve rapidly in Sn solders. The increase of Cu dissolution with increasing temperature leads to a decline of Ag solubility in Sn-3.5Ag, which, in turn, causes more Ag_3Sn particles to precipitate in the solder matrix. In addition to these fine Ag_3Sn precipitates, a number of large intermetallic bands of the same composition as the Ag_3Sn

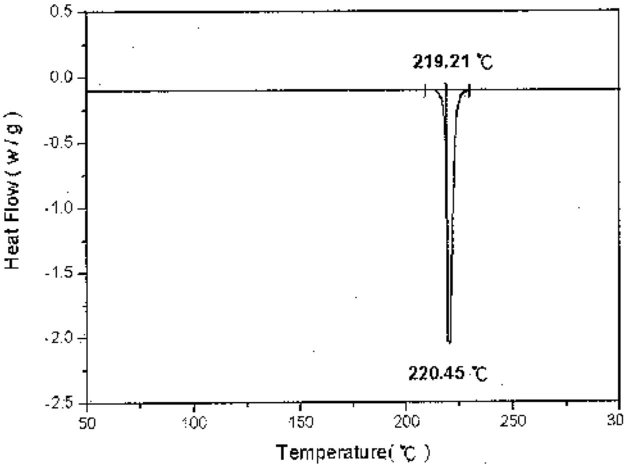

Fig. 2. DSC analysis of the eutectic Sn-3.5Ag solder.

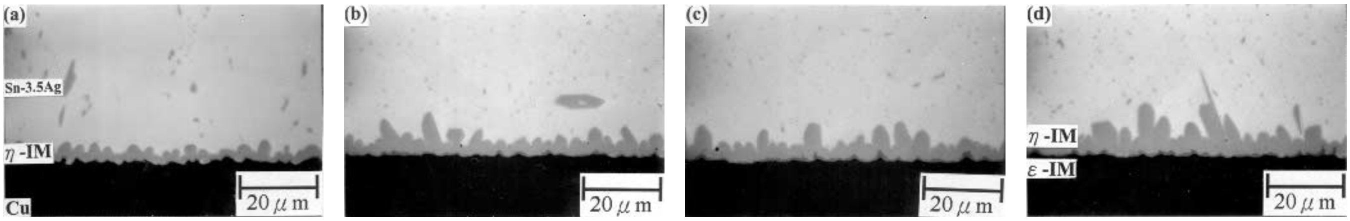

Fig. 3. Morphology of the intermetallic compounds formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates at 250°C for (a) 30 min, (b) 45 min, (c) 60 min, and (d) 75 min.

Table I. Chemical Compositions (At.%) of Intermetallic Compounds (IMs) Formed during Interfacial Reactions between Liquid Sn-3.5Ag Solders and Cu Substrates at Various Temperatures

Temperature	IM Positions	IM Phases	Cu	Sn	Ag
250°C	Sn-3.5Ag/Cu interface	η phase	54.40	45.39	0.31
		ε phase	75.21	24.70	0.09
	Sn-3.5Ag solder	η phase	54.25	45.42	0.33
		ε phase	—	—	—
300°C	Sn-3.5Ag/Cu interface	η phase	54.92	44.80	0.28
		ε phase	74.61	25.27	0.12
	Sn-3.5Ag solder	η phase	54.40	45.23	0.37
		ε phase	—	—	—
375°C	Sn-3.5Ag/Cu interface	η phase	55.15	44.56	0.29
		ε phase	75.85	24.08	0.08
	Sn-3.5Ag solder	η phase	54.52	45.18	0.30
		ε phase	—	—	—

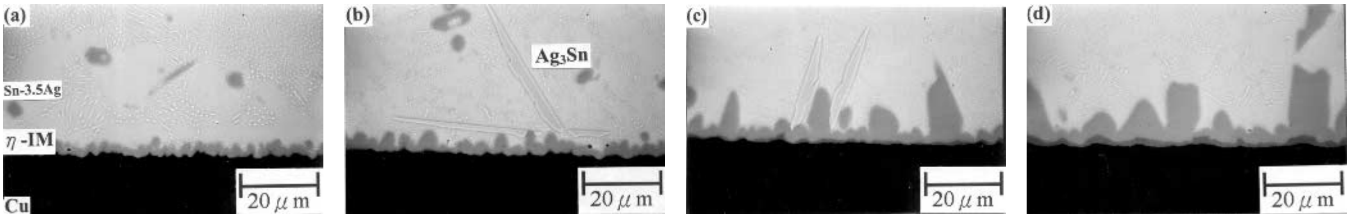

Fig. 4. Morphology of the intermetallic compounds formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates at 300°C for (a) 10 min, (b) 15 min, (c) 30 min, and (d) 60 min.

fine particles can also be found in Fig. 4, which tend to appear in the vicinity of interfacial η intermetallics. The formation of such intermetallic bands is believed to be a result of the increase in Cu dissolution at higher temperatures that simultaneously triggers the decrease of the Ag solubility in solder. Consequently, excessive Ag precipitates out to form large intermetallic bands during the solidification of the Sn-3.5Ag solder. The precipitation of fine Ag_3Sn particles can strengthen the solder matrix, while the appearance of large Ag_3Sn intermetallic bands is known to reduce the fatigue resistance in solder joints.[17] The severe rate of Cu dissolution into the solder can be further evidenced by Fig. 5, as the original interface has been marked by partial surface sputtering of a Ta thin film on the Cu substrate. The interface migrates toward the Cu substrate. At the migrating interface, scallop-shaped η intermetallics grow toward the solder matrix where many fine Ag_3Sn particles are dispersed. Along with the formation of interfacial intermetallic scallops, the dissolved Cu atoms precipitate to form coarse islands in the solder. In the vicinity of these coarse η-phase islands, Ag_3Sn precipitation-free zones can be observed.

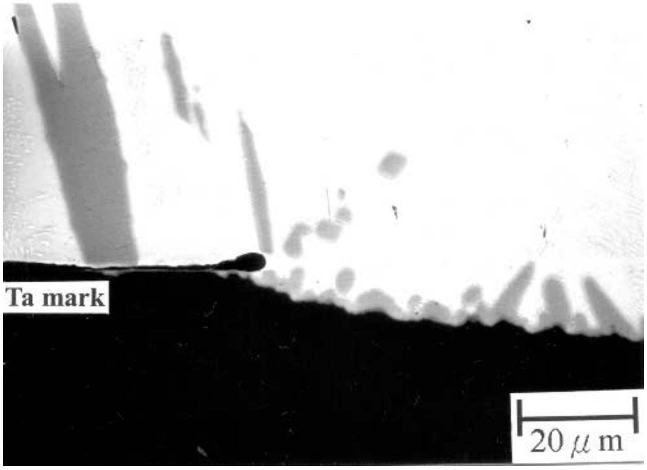

Fig. 5. Interface migration during the reaction between the liquid Sn-3.5Ag solder and Cu substrate at 300°C for 30 min.

Figures 6 and 7 reveal the dramatic growth of scallop-shaped η intermetallics with reaction time

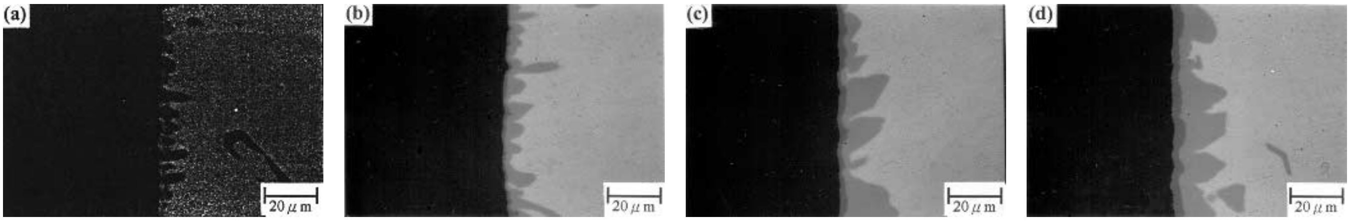

Fig. 6. Morphology of the intermetallic compounds formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates at 325°C for (a) 15 min, (b) 30 min, (c) 60 min, and (d) 120 min.

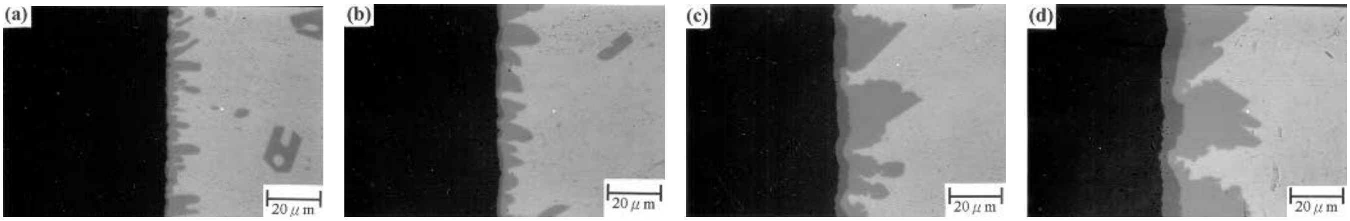

Fig. 7. Morphology of the intermetallic compounds formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates at 350°C for (a) 15 min, (b) 30 min, (c) 60 min, and (d) 120 min.

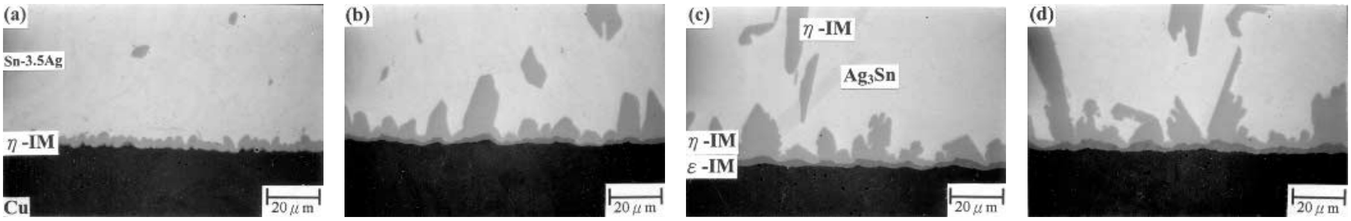

Fig. 8. Morphology of the intermetallic compounds formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates at various temperatures for 30 min: (a) 275°C, (b) 325°C, (c) 350°C, and (d) 375°C.

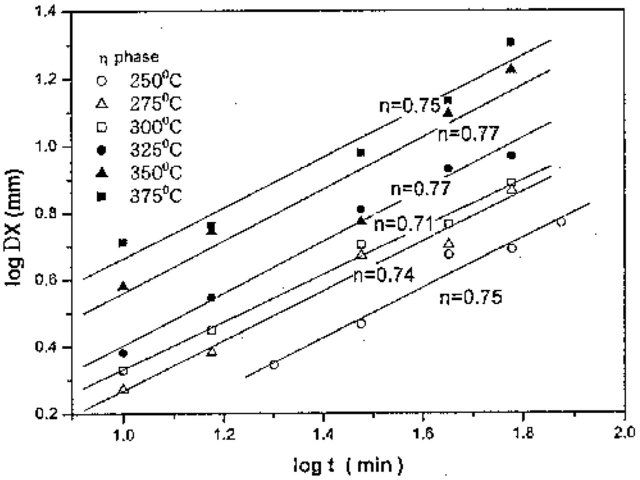

Fig. 9. Log plot of the thickness of η-$Cu_6(Sn_{0.993}Ag_{0.07})_5$ intermetallic compounds formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates as a function of reaction time.

at higher temperatures. It is worth noticing that the η-intermetallic compounds exhibit a tendency to elongate into the solder matrix without narrowing the grooves between intermetallic scallops. Figures 6 and 7 also show that a certain amount of coarse η-intermetallic scallops float into the solder matrix. It is believed that the detachment of these η-intermetallic islands from the interfaces into the solder matrix keeps the grooves between the remaining interfacial η scallops "unclosed." Such an "unclosed-groove" mechanism for intermetallic growth during soldering reactions is further verified in Fig. 8, as the grooves exist even up to the temperature of 375°C in spite of the growth of interfacial intermetallics, which is correlated to the detachment and floating of some η-intermetallic islands into the solder matrix. From Figs. 6–8, the growth profile for the reaction fronts of ε intermetallics coincides with that for η scallops, i.e., the ε intermetallics at the top of the η scallops tend to grow faster, while the ε intermetallics that remain behind the grooves are much thinner.

Figure 9 shows log plots for the thickness of η-$Cu_6(Sn_{0.993}Ag_{0.007})_5$ intermetallics formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates at various temperatures as a function of reaction time. The slopes in the plots give the n values of the kinetic relation: $\Delta X = t^n$. The results indicate that the n values range from 0.74 to 0.77, with an average of 0.75. The reactions do not quite follow the parabolic law (diffusion controlled). The nonparabolic growth kinetics of η intermetallics at $Sn\text{-}3.5Ag_{(l)}/Cu_{(s)}$ interfaces should be related to the presence of the liquid grooves between η-intermetallic scallops during soldering reactions throughout the temperature range of 250–375°C. In this case, Cu dissolves into the grooves and diffuses through those liquid paths to

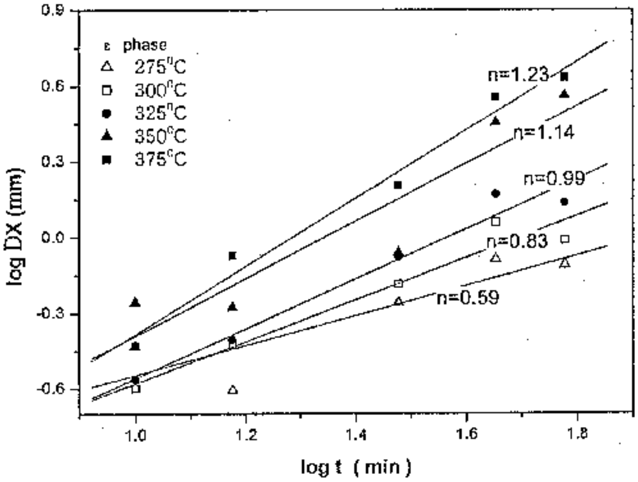

Fig. 10. Log plot of the thickness of ε-$Cu_3(Sn_{0.996}Ag_{0.004})$ intermetallic compounds formed during the interfacial reactions between liquid Sn-3.5Ag solders and Cu substrates as a function of reaction time.

react with Sn atoms at the front of the η scallops. For the solid/solid interfacial reactions of Sn/Cu couples, parabolic growth kinetics has often been reported. It is the absence of such liquid grooves (fast diffusion paths) that should be responsible for this disparity in growth kinetics.

The n values for the growth kinetics of ε-$Cu_3(Sn_{0.996}Ag_{0.004})$ intermetallics were calculated from the log plots in Fig. 10, which range from 0.59 to 1.23 (average 0.96). The linear kinetic relation reveals that the reaction is interface-controlled. The formation of ε-$Cu_3(Sn_{0.996}Ag_{0.004})$ intermetallic compounds is known to result from the reaction: $Cu(Sn,Ag) + 9Cu \rightarrow Cu_3(Sn,Ag)$. A comparison of Fig. 4a with d shows that the Cu fronts (η intermetallic/Cu substrate interfaces) are quite uneven (Fig. 4a) before the formation of ε intermetallics, but with the appearance of the ε intermetallics (viewed as ε intermetallic/Cu substrate interfaces in Fig. 4d), they are much smoother. This phenomenon implies that the Cu atoms have been reserved originally in the Cu hills beneath the η scallops and react later with η intermetallics to create the ε intermetallics. The rate-limiting step in the formation of ε intermetallics is, therefore, the local release of Cu atoms from the Cu hills into the η scallops and explains the resultant interface-controlled reaction for this case.

In a study of interfacial reactions between liquid Sn-37Pb solders and Cu substrates, Kim et al.[8] and Kim and Tu[9] found that the growth of Cu_6Sn_5 intermetallic compounds followed the relation $\Delta X = t^{1/3}$, they attributed such growth kinetics of intermetallics at the Sn-37Pb/Cu interfaces to the ripening reaction of Cu_6Sn_5 scallops. The soldering reactions in our case were conducted at much higher temperatures for longer times when compared with those in the study of Kim and Tu,[9] and the η-intermetallic scallops have anisotropically elongated toward the solder matrix, strongly indicative of the likely presence of the ripening effect during the earlier stages of the reactions. However, certain η intermetallics can be extruded out of the interfaces through the ripening of neighboring scallops, resulting in the appearance of lengthened intermetallic scallops at the interfaces together with the grooves left in between. The discrepancy between the results presented here and the study of Kim and Tu[9] on intermetallic growth kinetics can thus be clarified.

On the other hand, Bader and Gust studied the growth kinetics of solid-liquid interdiffusion between Cu and Sn thin films.[10] The Cu_6Sn_5 intermetallic compound was reported to grow in the ratio of $(t)^n$, where n was given as 0.20 and 0.25, respectively, for the reaction temperatures of 240°C and 300°C. According to their explanation, Cu and Sn atoms diffused through the grooves between the Cu_6Sn_5 crystallites at the onset of the $Cu_{(s)}/Sn_{(l)}$ interfacial reactions. Concurrent with the growth of Cu_6Sn_5, the grooves become narrower, and the diffusion of Cu and Sn slows down. It is reasonable for the resulting n values to become smaller than 0.5. However, it is invalid to apply their conclusion to the bulk solder case in our study. As shown in Figs. 6 and 7, the grooves stay unclosed because of the floating of certain η-intermetallic scallops into the liquid Sn-3.5Ag solder matrix. The fast diffusion paths for Cu atoms exhibit little change with the gaining of reaction time, which helps explain away the disparity in our study and Bader and Gust's result of intermetallic growth kinetics.

Liang et al.[18] studied the liquid-solid reactions of Cu/Sn/Au thin-film couples at temperatures between 250°C and 400°C from 10 min to 40 min. Owing to the low thickness of liquid Sn (4 μm), the η-intermetallic scallops could not be stripped away, leaving the grooves along the interface "closed" after such prolonged reactions. In this case, the reaction-controlling step in the growth of Cu_6Sn_5 intermetallic compounds was the diffusion of Cu and Sn atoms through the continuous Cu_6Sn_5 layer.

Bae and Kim[11] investigated the interdiffusion process during the soldering reactions between liquid Sn-3.5Ag solders and Cu substrates at 270°C and 350°C for 3–10 min. They found Sn played the dominant diffusion role in intermetallic formation, so was the case for solid/solid reactions at Sn/Cu interfaces. Although kinetics data is lacking to shed some light in the discrepancy between their results and ours, it should be pointed out that the Ag content of their η intermetallics at Sn-3.5Ag/Cu interfaces ranges from 0.66 at.% to 0.97 at.% (about threefold more than what our study obtains, as shown by Table I). In their case, the Ag_3Sn precipitation was absent, replaced by an increase in the Ag content of the solder in the vicinity of interfacial η intermetallics to the relatively high values of 9.51–11.03 at.%. In our case, the as-cast solder matrix contains only 0.60 wt.% (0.67 at.%) Ag because of the precipitation of Ag_3Sn. After soldering reaction, our solder matrix contains 1.59 wt.% (1.83 at.%) Ag and 0.11 wt.% (0.21 at.%) Cu. Because the element Ag has been reported to impact Cu dissolution in Sn,[19] the disparity in the Ag content of the solder matrix may be responsible for the different mechanisms for intermetallic formation in the two studies.

CONCLUSIONS

During the liquid-solid reactions between Sn-3.5Ag solders and Cu substrates at temperatures ranging from 250°C to 375°C, Cu dissolution into the solder causes the original interfaces to migrate toward the Cu substrates. Along with the formation of scallop-shaped η-$Cu_6(Sn_{0.993}Ag_{0.007})_5$ and ε-$Cu_3(Sn_{0.996}Ag_{0.004})$ intermetallics, fine Ag_3Sn particles and coarse η-intermetallic islands in large quantities appear in the solder matrix. At temperatures greater than 300°C, large Ag_3Sn intermetallic bands can be found in the solder. Kinetics analyses show that the intermetallic growth at Sn-3.5Ag/Cu interfaces follows the relation: $\Delta X = t^n$, where the n values for η and ε intermetallics are 0.75 and 0.96, respectively. These results disagree with the parabolic intermetallic-growth kinetics reported by many studies on the solid-solid interfacial reactions of Sn-Cu couples. The deviation in this study can be attributed to the unclosed liquid grooves between intermetallic scallops, which act as fast diffusion paths for Cu atoms to react with solders at the intermetallic fronts. The discrepancy in our research results of reaction kinetics and those reported by Kim et al. and Bader and Gust for liquid-solid reactions between Sn-37Pb (or Sn) solders and Cu substrates can also be attributed to varied reaction conditions leading to varied effects of liquid grooves upon the intermetallic growth.

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