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Interfacial Reactions Between Liquid Sn-8Zn-3Bi Solders and Cu Substrates

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The morphology and growth kinetics of intermetallic compounds formed during the soldering reactions between Sn-8Zn-3Bi and Cu substrates at various temperatures ranging from 225 to 350 °C were investigated. The results indicated that a planar layer of $Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$ (γ phase) along with a great number of scallop-shaped intermetallic compounds $Cu_{19.3}Zn_{77.8}Sn_{2.9}$ (ε phase) appeared at the interfaces at temperatures lower than 325 °C. At temperatures higher than 325 °C, the interfacial intermetallics of a composition similar to the planar intermetallics appeared in cluster shape. Kinetics analysis indicated that the intermetallic growth was diffusion-controlled with activation energy of 24.6 KJ/mol.

Keywords intermetallic compounds, kinetics analysis, lead-free solder, soldering reaction

1. Introduction

Eutectic Sn-Zn solder has a melting point quite like that of the traditional Sn-37Pb solder, demonstrating that it has advantages fit for Pb-free solders. Sn-Zn solders also claim the merits of low cost, high strength, and longer fatigue life.[1,2] During the solid/solid interfacial reactions between Sn-Zn solders and Cu substrates, a γ-Cu_5Zn_8 intermetallic compound has been reported by Lee et al.[3] and Yoon et al.[4] Suganuma et al.[5] have investigated the soldering reactions between Sn-Zn solders and Cu substrates at temperatures ranging from 230 to 280 °C for 5-35 min and have found three layers of intermetallic compounds (γ-Cu_5Zn_8, β′-CuZn, and an unknown thin-layer phase) formed at the interfaces. Recently, Chan et al.[6] showed that the intermetallic compound γ-$Cu_{33.4}Zn_{66.5}Sn_{0.1}$ of a planar shape, accompanied with a small amount of scallop-shaped intermetallic phase (ε-$Cu_{17.9}Zn_{81.9}Sn_{0.2}$), was formed at the interface between liquid Sn-9Zn solder and Cu substrate.

The melting point can be lowered by adding Bi into Sn-Zn solders,[7] and bismuth can also improve on the wettability and corrosion resistance of the Sn-Zn solders.[8] However, the mechanical properties of the solder joints might be degraded due to the existence of a Bi-rich phase in Bi-containing solders.[9] Harris reported that a γ-Cu_5Zn_8 intermetallic compound was formed at the Sn-8.5Zn-5.5Bi/Cu interface after aging at 125 °C for 10 days.[8] For the interfacial reaction between Sn-9Zn-1Bi-5In solder and Cu substrate, a similar intermetallic phase (γ-Cu_5Zn_8) was found by Yoon et al.[9] The morphology and growth kinetics of intermetallic compounds during the soldering reaction between liquid Sn-8Zn-3Bi and Cu substrate are investigated in this study.

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2. Experimental

The Sn-8Zn-3Bi solder was prepared from 3NSn, 3NZn, and 3NBi under 10^{-5} torr vacuum. The ingot was rolled into 0.2 mm thick foil. Copper substrates (8 × 2mm) were cut from a 1 mm thick 3N copper plate, ground with 1500 grit SiC paper, and polished with 1 μm Al_2O_3 powder. Before the soldering reaction, substrates were dipped in a rosin mildly activated (RAM) type flux. The Sn-8Zn-3Bi solder foils were then placed on Cu substrates and heated in an infrared (IR) furnace under a vacuum of 10^{-3} torr at temperatures ranging from 225 to 350 °C for various time periods. After reaction, the specimens were cross-sectioned, ground with SiC paper, polished with 1 and 0.3 μm Al_2O_3 powders, and observed by scanning electron microscopy (SEM). The compositions of the intermetallic compounds formed during the reactions were analyzed by electron probe microanalysis (EPMA). For kinetics analysis, the average thicknesses of the intermetallic compounds were also measured by SEM. Ta thin films were partially sputter-deposited over certain copper substrates, which act as markers for the original interfaces during the soldering reactions.

3. Results and Discussion

The microstructure of the as-cast Sn-8Zn-3Bi solder is shown in Fig. 1. A large amount of plate-like Zn-rich precipitates (shown in black) are seen embedded in the β-Sn matrix (in gray). Adjacent to a small number of Zn-rich precipitates, fine particles of Bi-rich precipitates (in white) can be observed. The melting temperature of the solder as measured by DSC is 197 °C, which is slightly lower than the eutectic point of Sn-9Zn alloy (199 °C). Figure 2 shows the typical morphology of the intermetallic compounds formed at the Sn-8Zn-3Bi/Cu interfaces during the soldering reactions at 225 °C for various time periods. A planar thick layer of intermetallic compound (IM1) is formed at the interface. EPMA analysis identifies the composition (at.%) of this intermetallic compound as Cu:Zn:Sn:Bi = 32.1:66.7:0.7:0.5, which is in the γ-phase field as shown in the Cu-Zn phase diagram. For most interfacial reactions of Sn-based solders (Sn-Pb, Sn-Bi, Sn-Ag, and Sn-Cu) with Cu substrates, scallop-shaped Cu_6Sn_5 intermetallic compounds are usually obtained.[10-13] According to the study of Kao on the soldering reactions of the Cu/Sn, Ni/Bi, and Cu/In systems, the appearance of scallop-shaped intermetallic compounds at interfaces is related to the rapid dissolution of substrate atoms into the liquid solder.[14] The appearance of planar-shaped $Cu_{32}Zn_{66.7}Sn_{0.7}Bi_{0.5}$ intermetallic compounds might be attributed to the rapid diffusion of Zn atoms conducive to the formation of the intermetallic layer, which is also predominant over the dissolution of Cu substrate into the molten solder. In Fig. 2, it can also be seen that ahead of the planar-shaped intermetallic compounds (IM1) there exist a certain number of scallop-shaped intermetallic compounds (IM2). The IM2 composition (at.%) as identified by EPMA is Cu:Zn:Sn = 19.3:77.8:2.9 (without Bi) of the ε-phase in the Cu-Zn phase diagram. The formation of such $Cu_{19.3}Zn_{77.8}Sn_{2.9}$ intermetallic compounds is triggered by further interfacial reaction of the former intermetallic compounds ($Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$) with liquid Sn-8Zn-3Bi solder.

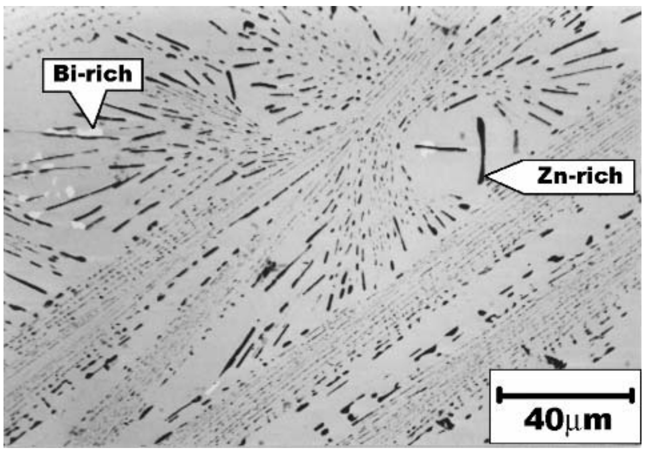

Fig. 1 Microstructure of the as-cast Sn-8Zn-3Bi solders in this study

Figure 3 shows the morphology of intermetallic compounds formed after interfacial reaction between liquid Sn-8Zn-3Bi solder and Cu substrate at various temperatures. It can be seen that the intermetallic compounds appear in planar shape (IM1) at lower temperatures, accompanied by many small scallop-shaped compounds (IM2) at the reaction fronts. However, at temperatures higher than 325 °C, the interfacial intermetallics ripen into a cluster shape. EPMA analysis indicates that these intermetallic clusters possess a composition similar to the planar intermetallics (IM1). The composition of the grooves between intermetallic clusters is similar to that of the solder matrix. The appearance of such cluster-shaped intermetallic compounds might be attributed to the increasing tendency of Cu dissolution into liquid Sn-8Zn-3Bi solder at higher temperatures, which induces the intermetallics to form irregularly at the interfaces as noted by Kao.[14]

From Fig. 2 and 3, the intermetallic compound $Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$ of the planar shape grows with increasing reaction temperature and time. The thickness (x) of such an intermetallic layer is measured and plotted against the square root of

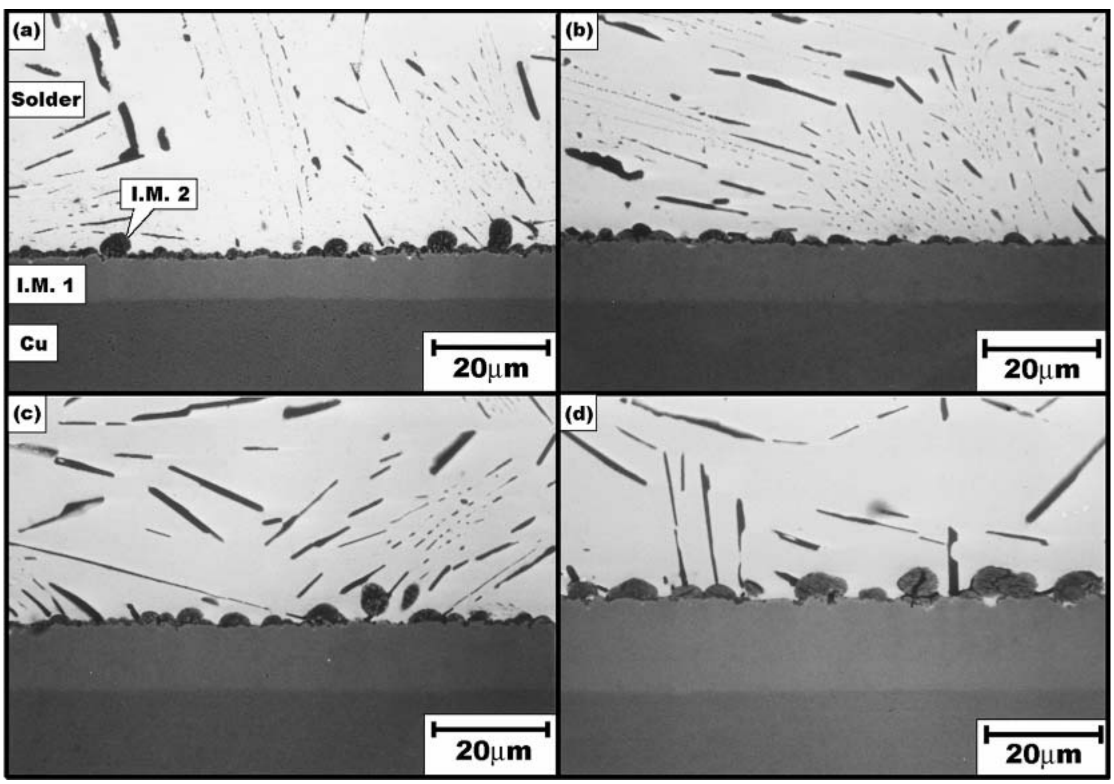

Fig. 2 Morphology of intermetallic compounds formed during the soldering reactions between liquid Sn-8Zn-3Bi and Cu substrates at 225 °C for various times: **(a)** 30 min, **(b)** 45 min, **(c)** 60 min, and **(d)** 90 min

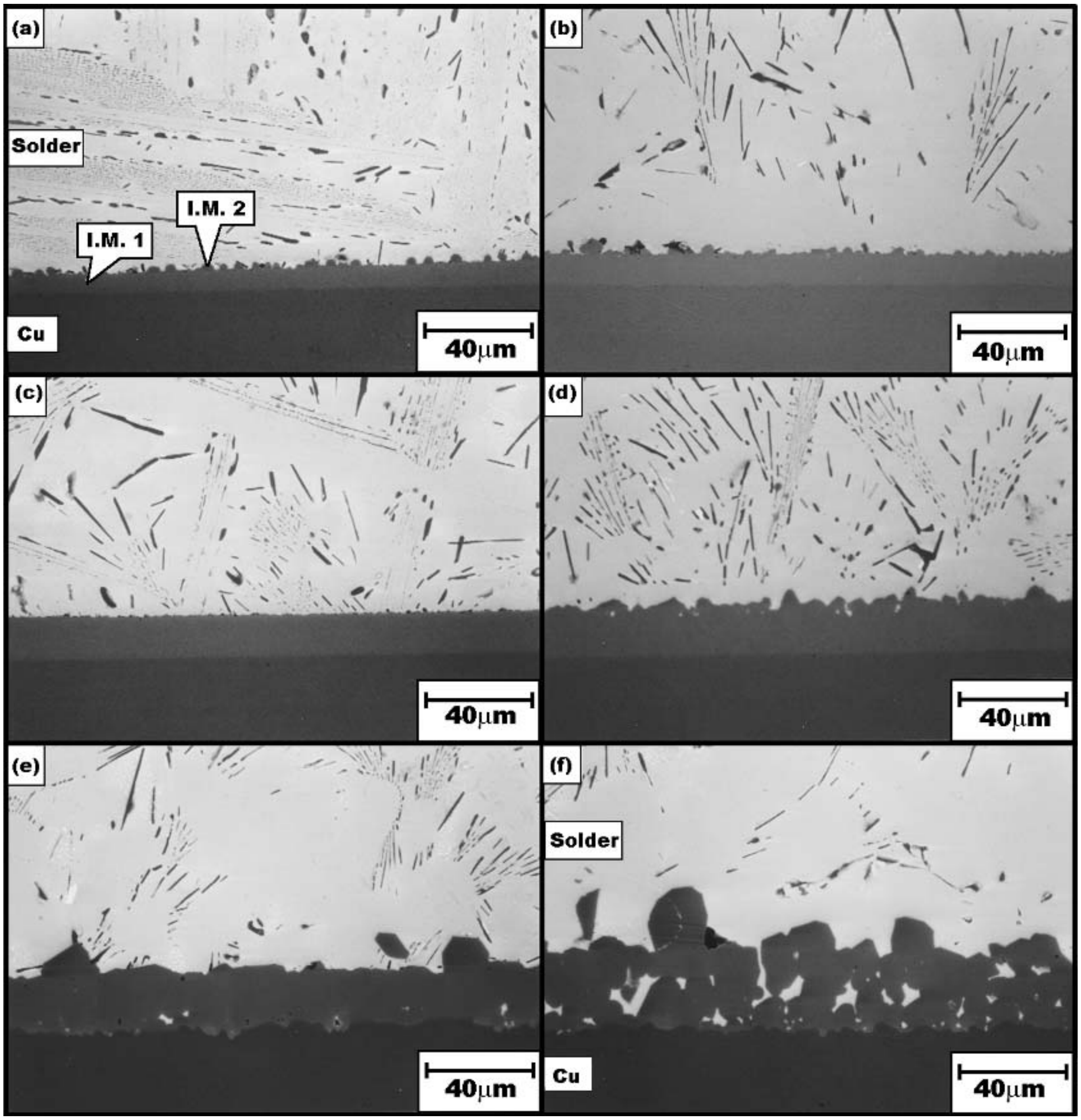

Fig. 3 Morphology of intermetallic compounds formed during the soldering reactions between liquid Sn-8Zn-3Bi and Cu substrates at various temperature for 30 min: **(a)** 240 °C, **(b)** 250 °C, **(c)** 260 °C, **(d)** 300 °C, **(e)** 325 °C, and **(f)** 350 °C

reaction time ($t^{1/2}$) as shown by Fig. 4, where the curves are expressed by a parabolic relation to indicate that the intermetallic growth is diffusion-controlled. The growth rate constants ($k_p = x/t^{1/2}$) at various temperatures are plotted in an Arrhenius diagram shown in Fig. 5. The slope of the Arrhenius plot gives the activation energy for the growth of the intermetallic compound $Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$, which is 24.6KJ/mol.

Through partial surface sputtering of the Ta thin film on the Cu substrates as a diffusion barrier for the Sn-8Zn-3Bi/Cu interfacial reactions, the original interfaces before soldering can be marked. Figure 6 shows that the reaction fronts of intermetallic compounds have migrated toward liquid solder and Cu substrate. The migration distance toward the solder is greater than that toward the Cu substrate in a ratio of 2.57. The ratio of the square of migration distances toward the solder to that toward the Cu substrate should correspond to the ratio of Zn and Cu diffusivities (D) in the $Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$ intermetallic compound, i.e.,

$$\frac{D_{Zn}\,(Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5})}{D_{Cu}(Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5})} = 6.6$$

4. Conclusions

Accompanied by a great number of scallop-shaped intermetallics $Cu_{19.3}Zn_{77.8}Sn_{2.9}$, planar-shaped intermetallic compounds $Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$ (γ phase) are formed during the interfacial reactions between liquid Sn-8Zn-3Bi solders and Cu substrates at temperatures ranging from 225 to 300 °C. As the reaction temperature is raised above 325 °C, the interfacial intermetallics of a composition similar to the planar

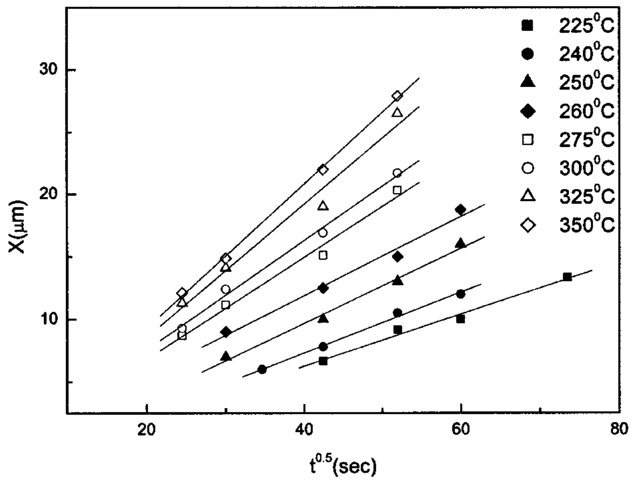

Fig. 4 Thickness (x) of the interfacial intermetallic compounds $Cu_{32.1}Sn_{0.7}Bi_{0.5}$ relative to the square root of time ($t^{1/2}$) for Sn-8Zn-3Bi/Cu soldering reactions

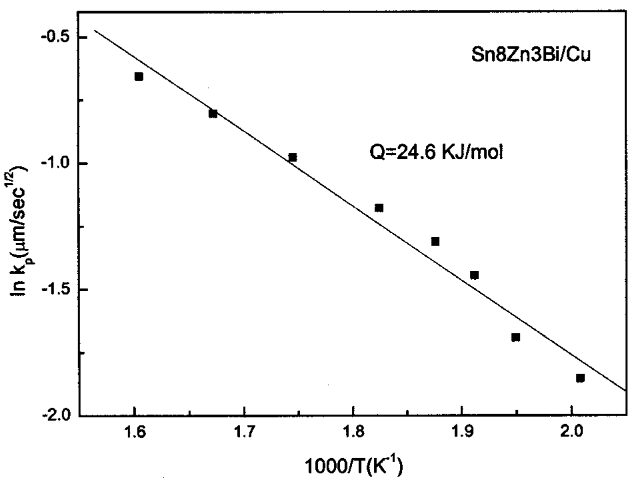

Fig. 5 Arrhenius plot of the growth rate constant (k_p) for the intermetallic compounds $Cu_{32.1}Sn_{0.7}Bi_{0.5}$ formed during the interfacial reactions between liquid Sn-8Zn-3Bi solders and Cu substrates

$Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$ intermetallic phase appear in the form of clusters.

The intermetallic growth follows a parabolic rate law and is diffusion-controlled. The activation energy as calculated from the Arrhenius plot of reaction rate constants is 24.6 KJ/mol. Through the employment of the Ta thin film to mark the original Sn-8Zn-3Bi/Cu interface before the soldering process, the reaction fronts of intermetallic compounds are found to migrate toward liquid solder and Cu substrate, and the ratio of Zn and Cu diffusivities in $Cu_{32.1}Zn_{66.7}Sn_{0.7}Bi_{0.5}$ is 6.6.

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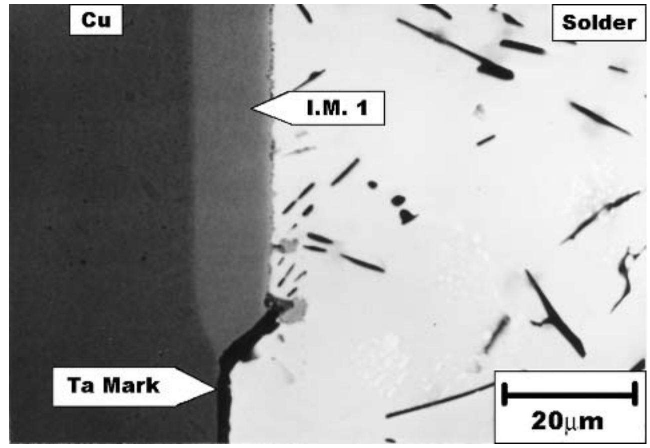

Fig. 6 Migration of traction fronts for the intermetallic growth during the Sn-8Zn-3Bi/Cu soldering reactions at 350 °C for 15 min; the original Sn-8Zn-3Bi/Cu interface was marked with partially sputtering deposited Ta thin films.

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