Phase Identification and Growth Kinetics of the Intermetallic Compounds Formed during In-49Sn/Cu Soldering Reactions

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For the application of In-49Sn solder in bonding recycled-sputtering targets to Cu back plates, the intermetallic compounds formed at the In-49Sn/Cu interface are investigated. Scanning electron microscopy (SEM) observations show that the interfacial intermetallics consist of a planar layer preceded by an elongated scalloped structure. Electron-probe microanalyzer analyses indicate that the chemical compositions of the planar layer and the scalloped structure are $Cu_{74.8}In_{12.2}Sn_{13.0}$ and $Cu_{56.2}In_{20.1}Sn_{23.7}$, respectively, which correspond to the $\varepsilon\text{-}Cu_3(In,Sn)$ and $\eta\text{-}Cu_6(In,Sn)_5$ phases. Kinetics analyses show that the growth of both intermetallic compounds is diffusion controlled. The activation energies for the growth of η- and ε-intermetallics are calculated to be 28.9 kJ/mol and 186.1 kJ/mol. Furthermore, the formation mechanism of intermetallic compounds during the In-49Sn/Cu soldering reaction is clarified by marking the original interface with a Ta-thin film. Wetting tests are also performed, which reveal that the contact angles of liquid In-49Sn drops on Cu substrates decline to an equilibrium value of 25°C.

Key words: Intermetallic compounds, In-49Sn/Cu, soldering

INTRODUCTION

The eutectic In49Sn solder possesses the advantages of higher ductility, better wettability, and longer fatigue life, merits suitable for the employment of In49Sn as a candidate for Pb-free solders in the electronics industry. On account of its low melting point, this eutectic solder has also been commonly used for bonding recycled-sputtering targets to their Cu back plates. During the soldering process, intermetallic compounds are formed at the In-49Sn/Cu interfaces, providing evidence of the interfacial reactions and connections between In-49Sn solders and Cu plates. However, too thick an intermetallic compound can result in brittle cracking at the interfaces. Therefore, phase identification and growth analysis of the reacted intermetallics during interfacial reactions between In-49Sn solders and Cu substrates provide vital links in such an application.

The interfacial reactions between eutectic In-Sn solders and Cu substrates have been studied.[1–7] Roming et al.[1] dipped Cu into In-50Sn molten solder and then aged the specimens in air at the tempera-

tures ranging from 60°C to 110°C. Two intermetallic compounds of $Cu_2(Sn,In)$ and Cu_2In_3Sn were found at the In-Sn/Cu interface. According to their report, the intermetallic growth was dominated by Cu_2In_3Sn, while the $Cu_2(Sn,In)$ phase was formed as the initial layer at the interface during the dipping process but failed to attain any further growth. The rate-limiting mechanism for the growth of the intermetallic layer changed with temperature. At higher temperatures, the intermetallic growth was limited by volume diffusion, while at lower temperatures, the growth kinetics was interfacial controlled. Vianco et al.[2] investigated the solid-state reactions between Cu and four solders (pure In, In-50Sn, pure Sn, and Pb-63Sn). They found that the intermetallic layer formed at the In-50Sn/Cu interface was more irregular than in the other three cases. In the case of In-50Sn/Cu interfacial reactions, the intermetallic compounds contained a thin $Cu_{17}Sn_9In_{24}$ layer near the solder matrix and a thicker $Cu_{26}Sn_{13}In_8$ layer on the side of the Cu substrate. In a study on the interfacial reactions and mechanical behaviors of solder joints on Cu substrates, Frear and Vianco[3] found that In-50Sn/Cu exhibited faster intermetallic

growth at 100°C in comparison with the case of Pb-63Sn/Cu. The intermetallic compound formed at the In-50Sn/Cu interface was Cu_2In_3Sn. In further studies on the microstructures and mechanical properties of In-Sn solder joints on Cu and Ni substrates, Freer and Morris[4–6] and Freer et al.[7] reported that a double layer of Cu_2In_3Sn and $Cu_2(Sn,In)$ intermetallic compounds was formed at the In-Sn/Cu interface. In contrast, a very thin intermetallic layer was found at the In-Sn/Ni interface, signifying a good barrier of Ni on the In-Sn solder.

In the literature, investigations of intermetallic compounds formed at the In-Sn/Cu interfaces have focused on cases of solid/solid reactions. However, this present study delves into the interfacial reactions between liquid In-49Sn solders and Cu substrates, and hence, the intermetallic compounds formed during such a liquid/solid state of reaction are identified, and their growth kinetics analyzed.

EXPERIMENTAL

Copper plates with a purity of 99.95% and thickness of 0.8 mm were cut to the size of 8 mm × 6 mm. They were ground with 1500-grit SiC paper and polished with 0.3-μm Al_2O_3 powder. The In-49wt.%Sn solder was prepared by vacuum melting into an ingot, homogenized at 100°C for 50 h, cold rolled into a 0.3-mm-thick foil, and then cut into a size of 7 mm × 5 mm. The solder foils were laid on the Cu plates and heated in an infrared furnace under a vacuum of 10^{-3} torr. Interfacial reactions were carried out at various temperatures ranging from 150°C to 400°C for various times. To eliminate the oxidation during soldering, a rosin mildly activated (RMA)-type flux was employed before testing.

For scanning electron microscopy (SEM) morphology observations, the reacted specimens were cut along the cross section, ground with 1500-grit SiC paper, and polished with 0.3-μm Al_2O_3 powder. The compositions of intermetallic compounds were analyzed by an electron-probe microanalyzer. To clarify the growth mechanism of intermetallic compounds during the interfacial reactions, the surface regions of the Cu plates were partially sputter-coated with a Ta-thin film that acted as a diffusion barrier between In-49Sn solders and Cu substrates. In so doing, the original In-49Sn/Cu interfaces could be marked.

To evaluate the wettability of In-49Sn solders on Cu substrates, the sessile-drop method was employed. The measurement of their contact angles was carried out in an infrared furnace under a vacuum of 10^{-3} torr using an in-situ video system.

RESULTS AND DISCUSSION

As shown in Fig. 1, the microstructure of the In-49Sn alloy before soldering reactions is composed of a lamellar Sn-rich γ phase and an In-rich β matrix. The In-49Sn eutectic solder possesses excellent wettability on Cu substrates (Fig. 2). The contact angles measured at temperatures above 200°C decline to
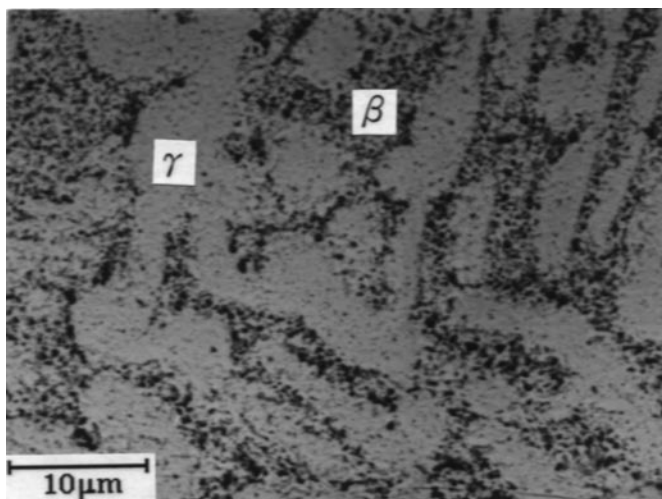

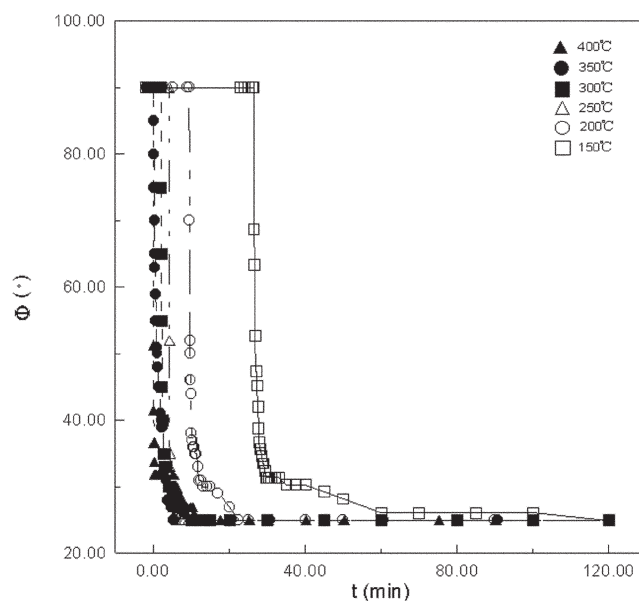Fig. 1. Microstructure of the eutectic In-49Sn solder.

Fig. 2. Contact angles (Φ) of In-49Sn solder drops on Cu substrates at various temperatures as a function of wetting time (t).

25° as the solder drops reach the melting point of 120°C. Below 200°C, the contact angles of the molten solder drops stay at 90° for several minutes and then collapse to attain the equilibrium value of 25°. The intermetallic compounds that appear at the In-49Sn/Cu interface after soldering reactions consisting of an elongated scalloped structure followed by a planar layer (Figs. 3 and 4). Chemical compositions of the intermetallic compounds formed at various temperatures are shown in Table I. The planar-intermetallic layer possesses a composition (at.%) of Cu:In:Sn = 74.8:12.2:13.0, which corresponds to the ε-Cu_3(In,Sn) phase. The composition of the elongated intermetallic scallops is Cu:In:Sn = 56.2:20.1:23.7, which corresponds to the η-Cu_6(In,Sn)$_5$ phase. It has been reported that the intermetallic compounds formed at the Sn/Cu,[8,9] Sn-Pb/Cu,[10,11] Sn-Ag/Cu,[12,13] Sn-Bi/Cu,[14–16] and Sn-Cu/Cu[17] interfaces consist of a
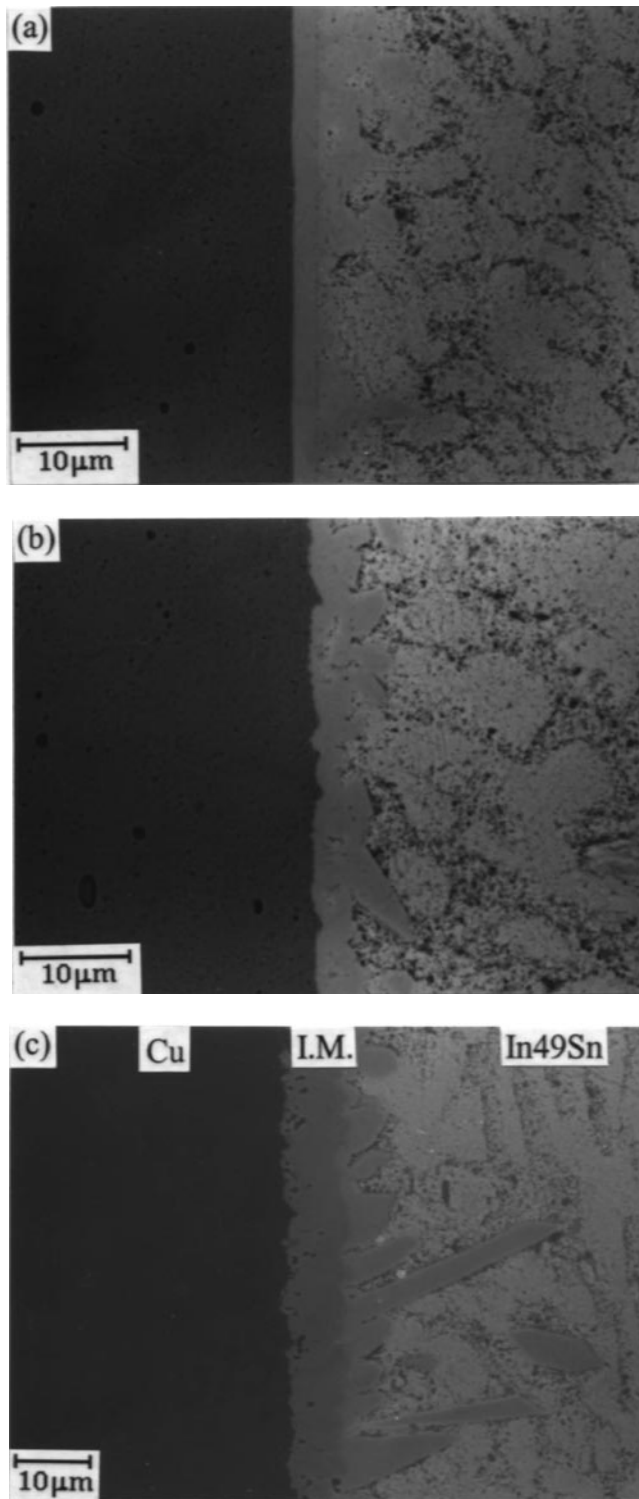
Fig. 3. Typical morphology of intermetallic compounds formed at In-49Sn/Cu interfaces after soldering reactions at various temperatures for 15 min: (a) 200°C, (b) 300°C, and (c) 400°C.
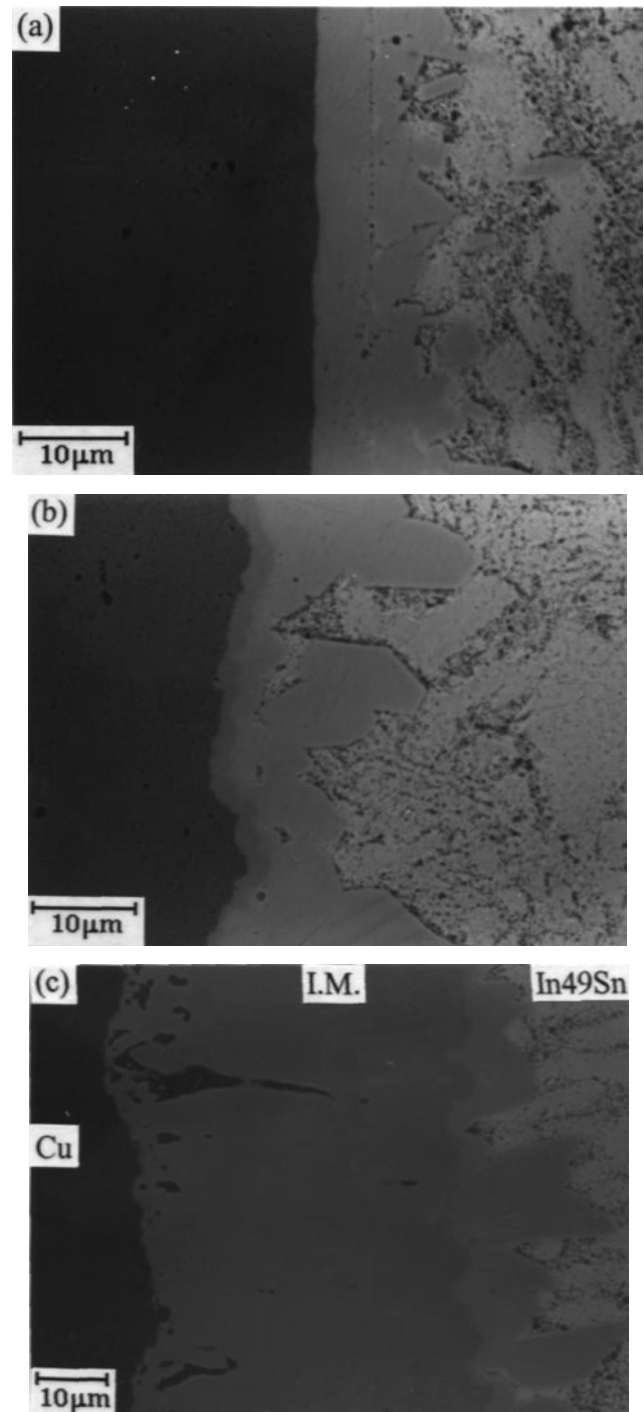

Fig. 4. Typical morphology of intermetallic compounds formed at In-49Sn/Cu interfaces after soldering reactions at various temperatures for 120 min: (a) 200°C, (b) 300°C, and (c) 400°C.

planar layer of Cu_3Sn and a scalloped structure of Cu_6Sn_5. The intermetallic phases formed during the In-49Sn/Cu soldering reaction in this study are similar to those in the preceding cases, except that the In element partially substitutes for Sn. From Table I, the Sn/In + Sn ratios in $Cu_3(In,Sn)$ and $Cu_6(In,Sn)_5$

intermetallic compounds are the same for the soldering reactions at the same temperatures. The Sn/In + Sn ratios in both intermetallic compounds decline slightly from 0.58 to 0.48 as the reaction temperature rises from 150°C to 400°C. The Sn/In + Sn ratios in the reacted intermetallics are near the atomic percentage (0.48) of Sn in the In-49wt.%Sn solder. In addition, the compositions of the intermetallic compounds formed during the In-49Sn/Cu soldering re-

**Table I. Chemical Compositions (at.%) of the Intermetallic Compounds
Formed During In-49Sn/Cu Soldering Reactions at Various Temperatures**

Temperature (°C)	ε Phase			η Phase		
	Cu	In	Sn	Cu	In	Sn
400	74.7	12.9	12.3	58.8	20.9	20.3
350	75.8	11.8	12.4	55.7	21.9	22.4
300	73.9	11.9	14.2	56.2	20.3	23.5
250	—	—	—	55.9	19.3	24.8
200	—	—	—	55.3	19.0	25.7
150	—	—	—	55.4	18.9	25.7

actions (in liquid/solid state) are different from those reported in the literature for thermal-aging reactions (i.e., solid/solid state) at In-49Sn/Cu interfaces, where the intermetallic compounds were found to be $Cu_2In_3Sn/Cu_2(Sn,In)$ or $Cu_{17}Sn_9In_{24}/Cu_{26}Sn_{13}In_8$ double layers.[1–7] The difference in the compositions of the double layers, as reported by Roming et al.[1] and Vianco et al.,[2] can be attributed to the disparate dipping conditions of both studies, which was already explained by Vianco et al.[2] It has been shown that the predominant phases for the growths of $Cu_2In_3Sn/Cu_2(Sn,In)$ and $Cu_{17}Sn_9In_{24}/Cu_{26}Sn_{13}In_8$ double layers are Cu_2In_3Sn and $Cu_{17}Sn_9In_{24}$, respectively. Obviously, either Cu_2In_3Sn[1,3–7] or $Cu_{17}Sn_9In_{24}$,[2] has grown close to the δ phase ($CuIn_2$) formed during the In/Cu interfacial reactions.[2] In contrast, the $Cu_3(In,Sn)$ and $Cu_6(In,Sn)_5$ intermetallics formed during the $InSn_{(l)}/Cu_{(s)}$ reactions in our study are consistent with the ε phase (Cu_3Sn) and the η phase (Cu_6Sn_5) present in the Sn/Cu interfacial reactions.[8,9] The results indicate that the low-melting-point In atoms become predominant to react with Cu during the thermal-aging reactions of $InSn_{(s)}/Cu_{(s)}$. However, the higher temperature range of $InSn_{(l)}/Cu_{(s)}$ soldering reaction causes the higher-melting-point Sn to become the predominate reaction agent.

From Figs. 3 and 4, it can also be seen that both types of intermetallic compounds grow with increasing reaction time and temperature. However, at temperatures below 300°C, the growth of scalloped intermetallics (the η phase) dominates over the planar-intermetallic layer (the ε phase). In contrast, the planar-intermetallic layer grows much more rapidly than the scallops at temperatures above 300°C. Consistent with the interpretation of Bader et al.[9] for the formation of Cu_3Sn intermetallic compounds at the Sn/Cu interface, the continuous $Cu_3(In,Sn)$ layer is also generated from the solid-state reaction between the scallop-shaped $Cu_6(In,Sn)_5$ intermetallics and the Cu substrate: $Cu_6(In,Sn)_5 + 9Cu \rightarrow 5Cu_3(In,Sn)$. The predominant growth of $Cu_3(In,Sn)$ intermetallic compounds at temperatures above 300°C could be attributed to the acceleration of the aforementioned solid-state reaction at higher temperatures because of its higher activation energies. Another explanation is that the maximum temperatures for $η(Cu_6Sn_5)$ and $ε(Cu_3Sn)$ phases in the Cu-Sn binary phase diagram are 415°C and 670°C,

respectively. The reaction temperatures above 300°C are near the maximum temperature of the η phase, resulting in a lower chemical driving force for the formation of this type of intermetallic compound.

Through partial surface sputtering of the Ta-thin film on the Cu substrate as a diffusion barrier, the original In-49Sn/Cu interface can be distinguished. It can be observed from Fig. 5a and b that the Cu substrate is rapidly consumed at the early stage of soldering reactions, which results in the appearance of a concave interface. However, the thickness of intermetallic compounds at the reacted interface is much less than the Cu thickness. The discrepancy is attributed to the severe spalling of intermetallic compounds away from the In-49Sn/Cu interface (Fig. 5c). With increased reaction time, the intermetallic compounds fill in the region where Cu is consumed and grow toward the Cu substrate. It is interesting to note in Fig. 5c and d that the migrating intermetallic compounds seem incapable of passing the original In-49Sn/Cu interfaces.

The growth kinetics for η- and ε-intermetallic compounds is estimated by measuring the migration distances of their respective reaction fronts, i.e., the η/solder and ε/η interfaces. In this way, the migration distance of the ε-reaction front is equal to its phase width, while the distance for the η-reaction front includes the width of the ε-intermetallic. It makes more sense using this method for kinetics analysis because the ε-intermetallic owes its growth to partial volume consumption of the η-intermetallic: $Cu_6(In,Sn)_5 + 9Cu \rightarrow 5Cu_3(In,Sn)$.

The measured migration distances (ΔX) of reaction fronts for η- and ε-intermetallics versus the square root of reaction time are plotted in Figs. 6 and 7, respectively. The migration of both reaction fronts follows a parabolic-rate law, implying that the growths of both intermetallics are diffusion controlled. From the curves in Figs. 6 and 7, the reaction constants ($kp = (\Delta X/t^{1/2})$) can be calculated and plotted in Fig. 8 by applying the Arrhenius relation. The activation energies for the growths of η- and ε-intermetallics, as obtained from the slopes of both Arrhenius plots, are 28.9 kJ/mol and 186.1 kJ/mol, respectively. The former value (28.9 kJ/mol) is consistent with the activation energy of Cu in liquid Sn (19.5 kJ/mol), as reported by Ma and Swalin.[18] The rate-limiting step for the growth of the η-inter-
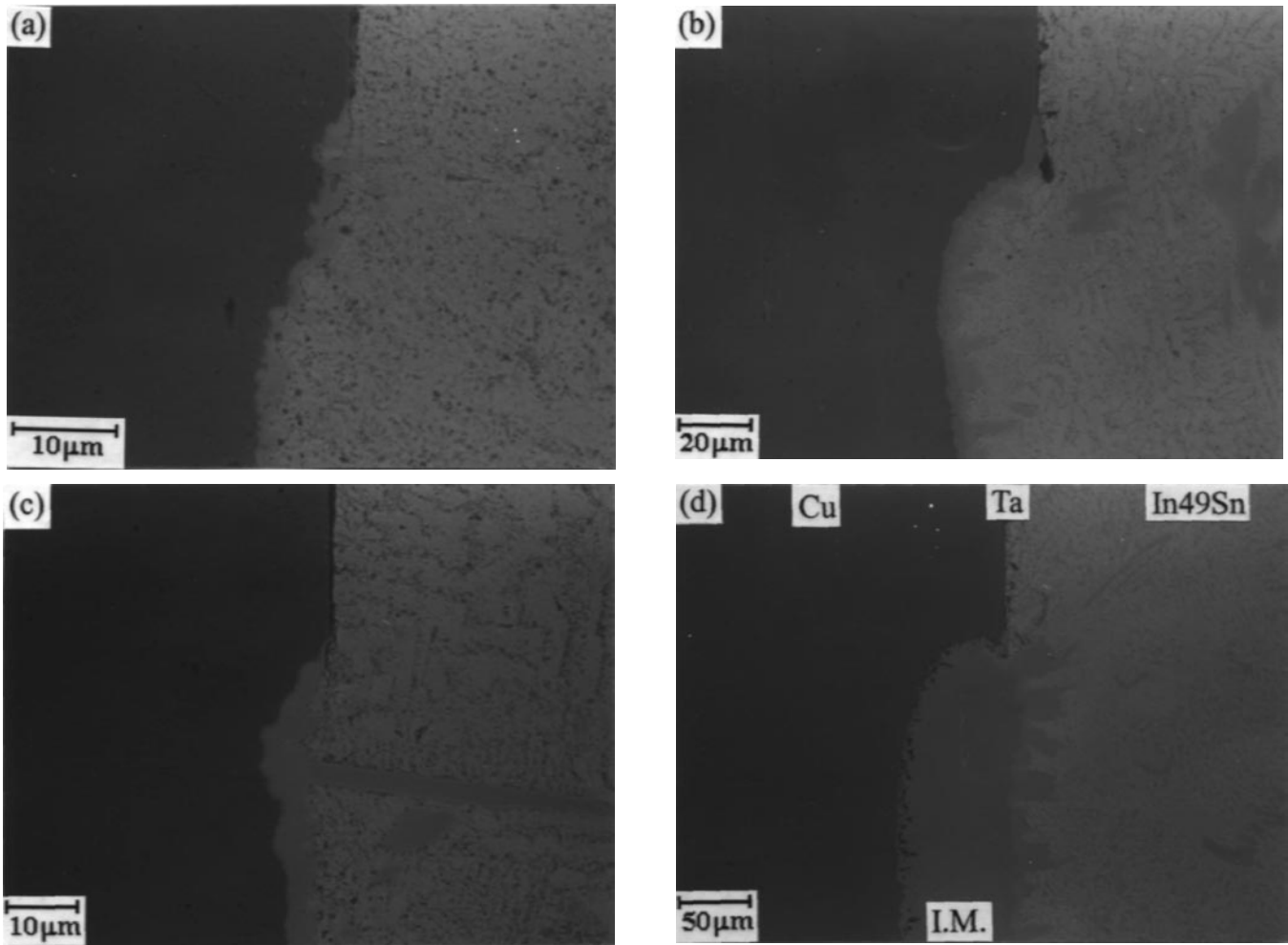
Fig. 5. Migration of intermetallic compounds during soldering reactions between In-49Sn solders and Cu substrates: (a) 250°C, 15 min; (b) 400°C, 15 min; (c) 250°C, 120 min; and (d) 400°C, 120 min. (The original In-49Sn/Cu interfaces are marked with Ta-thin films.)
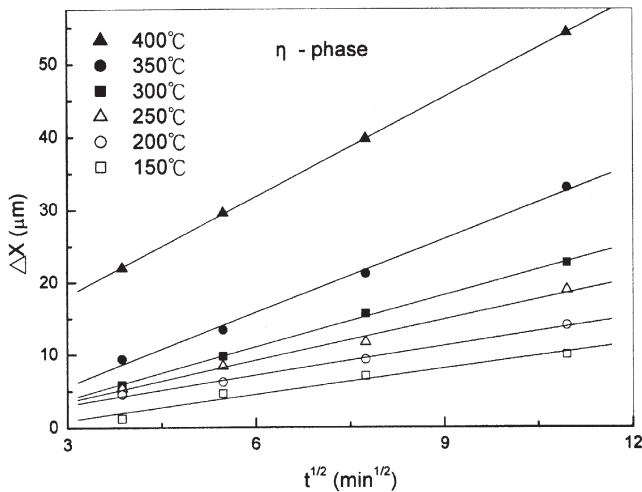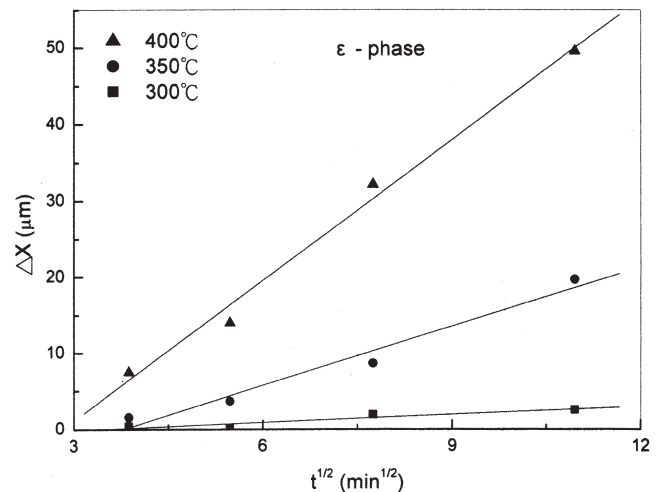

Fig. 6. Migration distance (ΔX) of the η-intermetallic compound formed at the In-49Sn/Cu interface as a function of the square root of time ($t^{1/2}$).

Fig. 7. Migration distance (ΔX) of the ε-intermetallic compound formed at the In-49Sn/Cu interface as a function of the square root of time ($t^{1/2}$).

metallic toward the In-49Sn solder is the diffusion of Cu dissolved near the η-reaction front into the surrounding liquid solder. The calculated activation energy for the growth of the ε-intermetallic (186.1 kJ/mol) is close to the activation energies for the lattice diffusion of Sn and In in bulk Cu (187.6 kJ/mol and 178.0 kJ/mol, respectively).[19,20] The growth of the ε-intermetallic is, therefore, believed to be con-
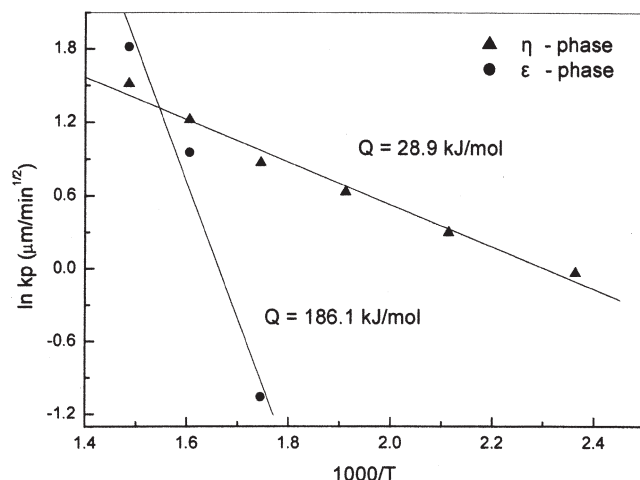
Fig. 8. Arrhenius plots of growth rate constants (k_p) for the inter-
metallic compounds formed during In-49Sn/Cu soldering reactions.

trolled by the lattice diffusion of Sn and In through
the intermetallic compounds. The much higher acti-
vation energy for the growth of the ε-intermetallic
than for the η-intermetallic can also explain why
the growth of the ε-intermetallic becomes predomi-
nant over the η-intermetallic at higher tempera-
tures.

CONCLUSIONS

Eutectic In-49Sn solder exhibits excellent wetta-
bility on a Cu substrate. During the In-49Sn/Cu sol-
dering reactions at temperatures ranging from
150–400°C, intermetallic compounds consisting of a
planar layer and an elongated scalloped structure
appear at the interface. The planar-intermetallic
layer possesses a composition of $Cu_{74.8}In_{12.2}Sn_{13}$,
which corresponds to the ε-Cu_3(In,Sn) phase. The
scallop-shaped intermetallic compound is identified
to be $Cu_{56.2}In_{20.1}Sn_{23.7}$, which corresponds to the η-
$Cu6$(In,Sn)$_5$ phase. In this study, the results ob-
tained from the In-49Sn/Cu soldering reactions (liq-
uid/solid) are different from those reported in other
published work[1–7] on the thermal aging of In-Sn/Cu
solder joints (solid/solid). The present experiments
also show that the ε-intermetallic grows faster than
the η-intermetallic at temperatures above 300°C. By
marking the original interface with a Ta-thin film,
the Cu substrate is consumed rapidly to form a con-
cave interface during the soldering reaction. As the
reaction time increases, the intermetallic com-
pounds fill in the region where Cu is consumed and
grow toward the Cu substrate. Kinetics analyses
show that the growth of both η- and ε-intermetallics
are diffusion controlled. The calculated activation
energy for the η-intermetallic growth is 28.9 kJ/mol,
which is relatively close to that for the diffusion of
Cu in liquid Sn (19.5 kJ/mol). The result implies
that the η-intermetallic growth is controlled by the
diffusion of dissolved Cu in the liquid solder. The ac-
tivation energy for the ε-intermetallic growth is
186.1 kJ/mol, which is consistent with the activation
energies for the lattice diffusion of Sn in Cu (187.6
kJ/mol) and In in Cu (178.0 kJ/mol). The ε-inter-
metallic growth is thus concluded to be the diffusion
of Sn and In in the intermetallic compounds.

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