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Effects of third element and surface finish on interfacial reactions of Sn–Ag–*x*Cu (or Ni)/(Cu or ENIG) solder joints

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ABSTRACT

In this study, we investigated the effect of the Cu content on the interfacial reactions between the Sn–Ag–*x*Cu solders and Cu substrate. In addition, we evaluated the effects of adding Cu or Ni to Sn–Ag solder on the interfacial reactions of the Sn–Ag–Cu (or Ni)/ENIG joints. The formation and growth of interfacial intermetallic compounds (IMCs) between the Ni-containing Sn–Ag–Ni solder and ENIG substrate were studied and the results were compared to the Sn–Ag–Cu/ENIG system. Increasing the amount of Cu added to the Sn–Ag solder significantly reduced the thickness of the Cu_3Sn IMC, while increasing that of the total Cu–Sn and Cu_6Sn_5 IMCs. $(Ni,Cu)_3Sn_4$ and Ni_3Sn_4 IMCs formed at the Sn–3.0Ag–0.5Cu/ENIG and Sn–3.0Ag–0.5Ni/ENIG interfaces, respectively. These two IMCs grew during isothermal aging and similar interfacial microstructures were found in the Sn–3.0Ag–0.5Cu (or Ni)/ENIG joints. Comparing the Sn–3.0Ag–0.5Cu/Cu and Sn–3.0Ag–0.5Cu/ENIG joints, the growth rate of the IMC layer for the Cu substrate was about 3.3 times faster than that for the ENIG substrate.

1. Introduction

Many researchers have tried to add minor elements to improve the properties of Sn–Ag solder [1–6]. They investigated the use of alloying elements such as Cu, Ni, Co, Sb, Bi, and so on, as a means of reducing the melting temperature of Sn–Ag solder, while simultaneously improving its mechanical properties. The results of these studies confirmed that certain composite solders exhibit the necessary combination of enhanced strength and other favorable mechanical properties required by the electronics industry. Among these alloying elements, Cu and/or Ni have primarily been chosen, owing to the formation of additional intermetallic phases that could improve the mechanical properties of the solder. The addition of small amounts of Cu was found to decrease the melting temperature and improve the wetting properties of the Sn–Ag solder [1,5]. In addition, Ni is commonly used to provide a diffusion barrier between Cu and Sn-based solder alloys, in order to prevent, or at least suppress, the formation of Cu_6Sn_5 and Cu_3Sn intermetallic compounds (IMCs). Ni is an effective additive, since the stable phases, which it forms in the Ni–Sn binary system, grow more slowly than the Cu–Sn IMCs.

In addition, the selection of an appropriate surface finish plays an important role in developing a reliable packaging technology. Cu is widely used in the under bump metallurgy and substrate metallization for flip-chip and ball-grid-array (BGA) applications. It is known that, at the solder/Cu interface, Sn reacts rapidly with Cu to form Cu–Sn IMC, which weakens the solder joints due to its brittle nature [7]. Therefore, electroless Ni(P) plating has been used as a diffusion barrier layer on the Cu bond pad for flip-chip and BGA packages, because of its low cost and simple process [3,8].

Generally, solder joints provide both electrical conductivity and mechanical strength and, consequently, play an important role in the connection of electronic components to printed circuit boards. In the development of package material systems, the joint reliability should be considered as one of the most critical criteria [9,10]. Since the joining process is a direct consequence of the interfacial reaction between the solder and substrate, understanding the interaction between such materials is an integral part of developing a reliable joining system. Many studies have been performed on the joint reliability and interfacial reaction between Pb-free solders and various surface finishes, such as Cu, Au/Ni/Cu and electroless nickel-immersion gold (ENIG), during reflow or aging [6–10]. Nevertheless, insufficient comparative studies have been done on the interfacial reactions of Sn–Ag–*x*Cu/Cu and Sn–Ag–Cu (or)Ni/ENIG solder joints. Therefore, in this study, we investigated the effect of the Cu content on the interfacial reactions between the Sn–Ag–*x*Cu solders and Cu substrate. In addition, we evaluated the effects of adding Cu or Ni to Sn–Ag solder on the interfacial reactions of the Sn–Ag–Cu (or Ni)/ENIG joints. The formation and growth of interfacial IMCs between the Ni-containing Sn–Ag–Ni solder and ENIG substrate were studied and the results were compared to

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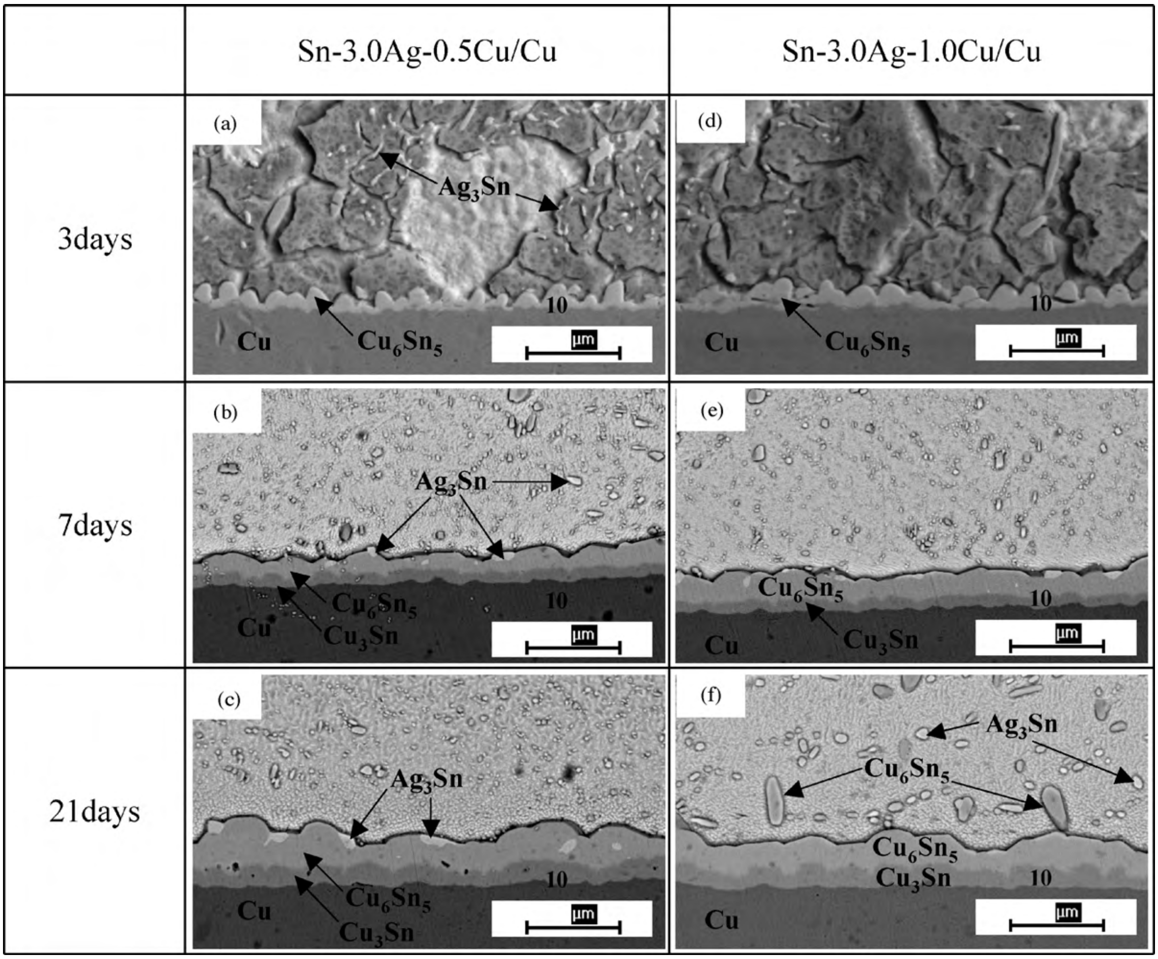


Fig. 1. Cross-sectional SEM images of the (a–c) Sn–3.0Ag–0.5Cu/Cu and (d–f) Sn–3.0Ag–1.0Cu/Cu interfaces aged at 150 °C for various times.

those obtained for the Sn–Ag–Cu/ENIG system. The effect of the surface finish on the growth kinetics of the interfacial IMCs of the Sn–Ag–Cu/Cu or ENIG joints is also discussed.

2. Experimental procedure

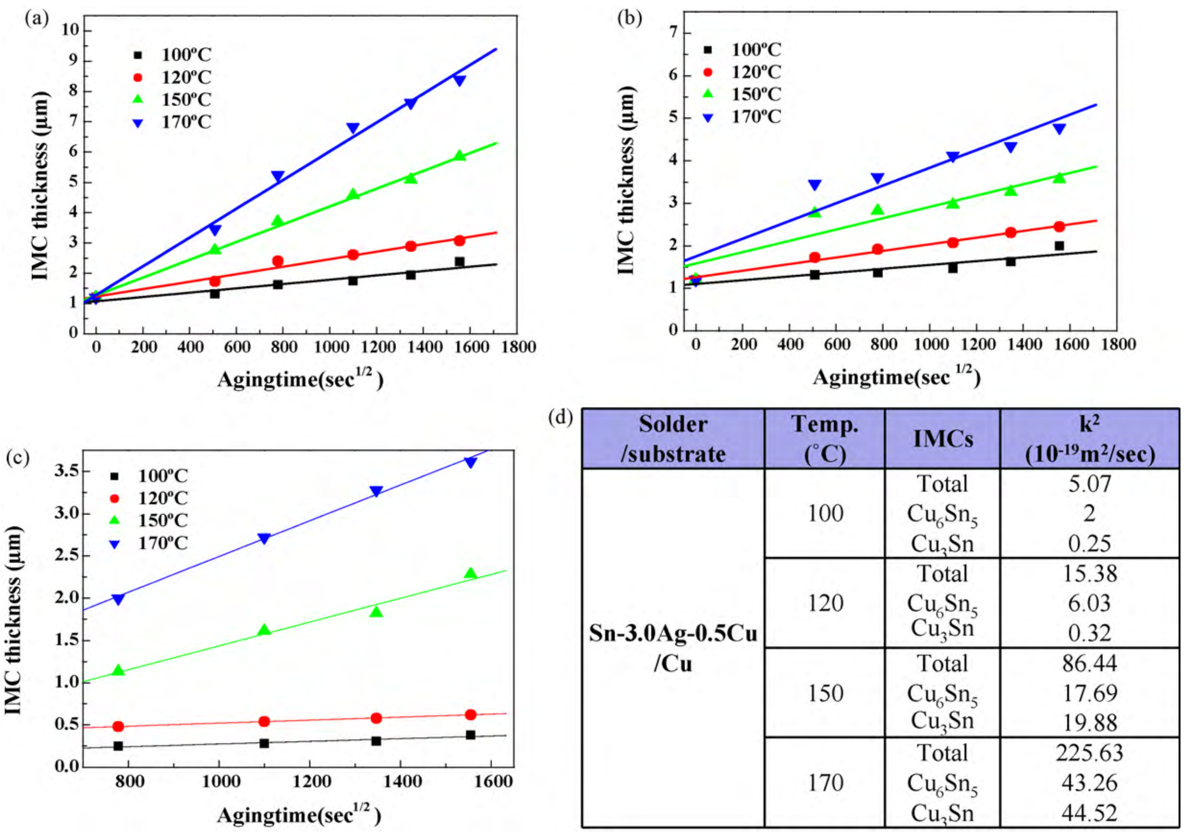
Four kinds of solder joints, Sn–3.0Ag–0.5Cu/Cu, Sn–3.0Ag–1.0Cu/Cu, Sn–3.0Ag–0.5Cu/ENIG and Sn–3.0Ag–0.5Ni/ENIG (in wt.%), were used in this study. Solder balls with a diameter of 500 μm were used in each case. The substrate was frame-retardant-4 (FR-4) with Cu bond pads which had a circular opening diameter of 460 μm. Two kinds of bond-pads (organic solderability preservative (OSP) finished Cu and ENIG plated Cu) were prepared. The ENIG plated Cu pad was constructed by electroless-plating an Au (0.15 μm)/Ni(P) (7 μm) layer onto the underlying Cu pad. Rosin mildly activated (RMA)-type flux was applied to the bond-pads and the solder balls were placed on the pads. Then, reflow was conducted in an infrared 4-zone reflow machine (RF-430-N2, Japan Pulse Laboratory Co. Ltd., Japan). The peak temperature and dwell time during reflow were 270 °C and 120 s, respectively. After the reflow process, the samples were cooled to room temperature. Then, each sample was cleaned with isopropyl alcohol (IPA).

To evaluate the interfacial reactions between the Sn–Ag–Cu (or Ni) solder alloys and Cu (or ENIG) substrates during the solid-state reaction, isothermal aging treatment was performed. The samples were aged at 100, 120, 150, and 170 °C for up to 28 days (4 weeks). After the reflow and aging treatment, the samples were prepared for the observation of the interface cross-section. The common metallographic practices, grinding and polishing, were used to prepare the samples. An etchant consisting of 95% C_2H_5OH-4% HNO_3-1% HCl was used to reveal the cross-sectional microstructure. The microstructures and chemical compositions were observed with a scanning electron microscope (SEM, Philips XL 40 FEG, The Netherlands) equipped with an energy dispersive X-ray spectroscope (EDX). The thickness of the interfacial IMC layer was evaluated using image analysis software to measure the total area of the intermetallic layer. The phase areas were divided by the interface length shown in the cross-section to yield the average layer thickness.

3. Results and discussion

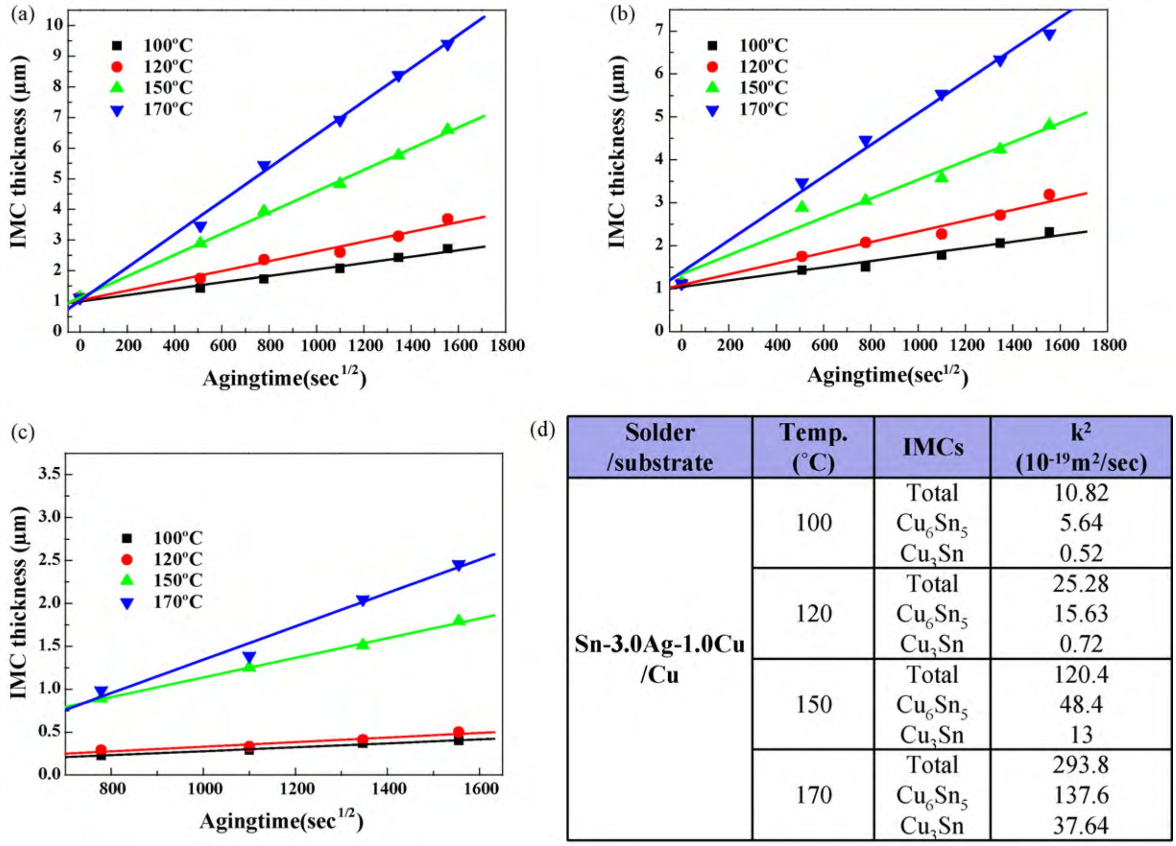
3.1. Sn–3.0Ag–0.5Cu/Cu vs. Sn–3.0Ag–1.0Cu/Cu

In order to evaluate the influence of the Cu content on the interfacial reactions of the Sn–Ag–*x*Cu/Cu joints, isothermal aging treatment was conducted. Recently, we investigated the interfacial reactions of Sn–3.0Ag–0.5Cu/Cu solder joints during isothermal aging, and the results [5] are used here only to provide a direct comparison between the Sn–3.0Ag–0.5Cu and Sn–3.0Ag–1.0Cu joints. The Sn–3.0Ag–(0.5 or 1.0)Cu/Cu interfaces were reflowed at 270 °C for 2 min. During their reflow, the solders were in the molten state and typical scallop-type Cu_6Sn_5 IMCs formed at the interfaces. Fig. 1 shows the cross-sectional SEM images of the Sn–3.0Ag–(0.5 or 1.0)Cu/Cu interfaces aged at 150 °C for different aging times. The interfacial structures of the two solder joints aged for 3 days, shown in Fig. 1(a) and (d), were similar to those of the as-reflowed samples. Only scallop-type Cu_6Sn_5 IMCs were detected at the interfaces. The Cu_6Sn_5 IMC layer of the Sn–3.0Ag–1.0Cu/Cu joint was slightly thicker than that of the Sn–3.0Ag–0.5Cu/Cu joint, due to the higher Cu content in the Sn–3.0Ag–1.0Cu solder. After aging at 150 °C for 7 days, Cu_3Sn IMC formed at the interface between the Cu_6Sn_5 IMC and Cu substrate, as shown in Fig. 1(b) and (e). Most Sn-based solder alloys form these two reaction layers (Cu_6Sn_5 and Cu_3Sn) at the interface between the solders and Cu substrate [11]. In addition, the morphology of the interfacial Cu–Sn IMC gradually changed from scallop-type to layer-type. The two IMC layers, Cu_6Sn_5 and Cu_3Sn, grew with increasing aging time. The interfacial



Solder /substrate	Temp. (°C)	IMCs	k^2 (10^{-19}m²/sec)
Sn-3.0Ag-0.5Cu /Cu	100	Total	5.07
		Cu_6Sn_5	2
		Cu_3Sn	0.25
	120	Total	15.38
		Cu_6Sn_5	6.03
		Cu_3Sn	0.32
	150	Total	86.44
		Cu_6Sn_5	17.69
		Cu_3Sn	19.88
	170	Total	225.63
		Cu_6Sn_5	43.26
		Cu_3Sn	44.52

Fig. 2. Thickness of the IMC layers formed at the Sn–3.0Ag–0.5Cu/Cu interface during isothermal aging: (a) total ($Cu_6Sn_5 + Cu_3Sn$), (b) Cu_6Sn_5, (c) Cu_3Sn and (d) calculated growth rate constants.



Solder /substrate	Temp. (°C)	IMCs	k^2 (10^{-19}m²/sec)
Sn-3.0Ag-1.0Cu /Cu	100	Total	10.82
		Cu_6Sn_5	5.64
		Cu_3Sn	0.52
	120	Total	25.28
		Cu_6Sn_5	15.63
		Cu_3Sn	0.72
	150	Total	120.4
		Cu_6Sn_5	48.4
		Cu_3Sn	13
	170	Total	293.8
		Cu_6Sn_5	137.6
		Cu_3Sn	37.64

Fig. 3. Thickness of the IMC layers formed at the Sn–3.0Ag–1.0Cu/Cu interface during isothermal aging: (a) total ($Cu_6Sn_5 + Cu_3Sn$), (b) Cu_6Sn_5, (c) Cu_3Sn and (d) calculated growth rate constants.

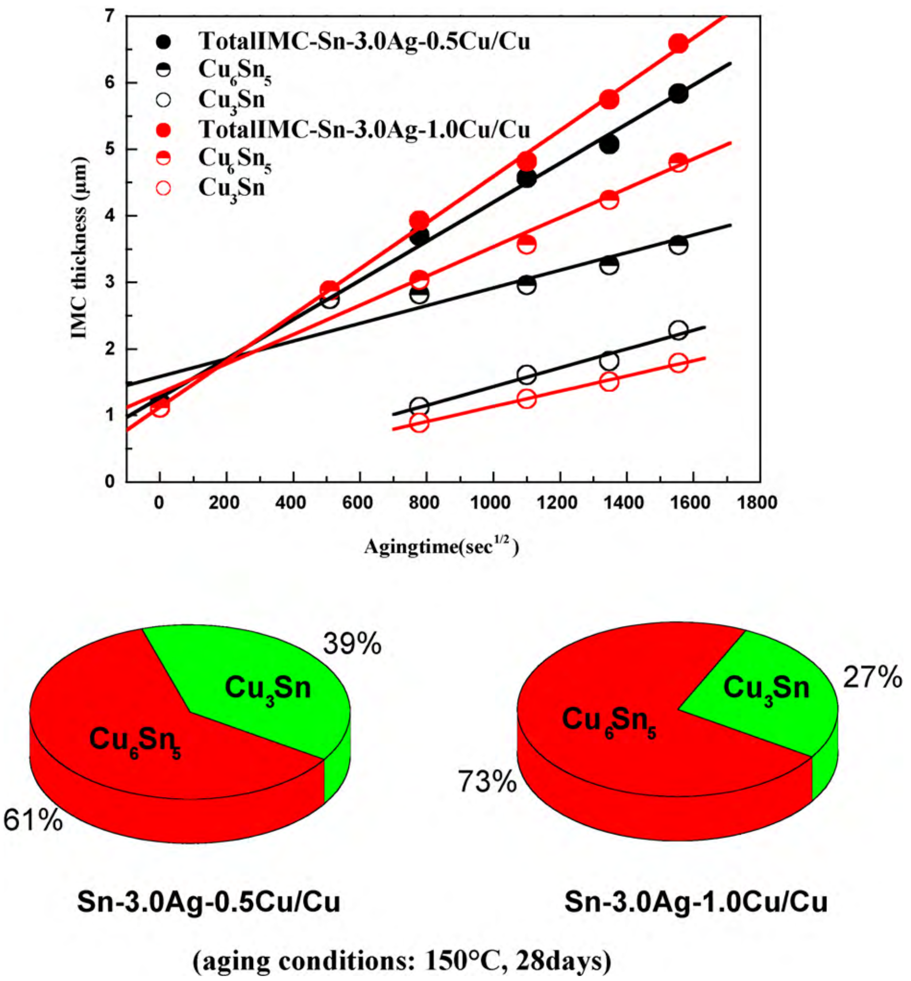


Fig. 4. (a) Thickness of the IMC layers formed at the Sn–3.0Ag–0.5Cu/Cu and Sn–3.0Ag–1.0Cu/Cu interfaces aged at 150 °C and (b) IMC portion after aging at 150 °C for 28 days.

reaction and IMC growth in this solder system are well-known and have been reported in previous studies [12,13]. Although not presented here, the joints aged at the other temperatures displayed similar characteristics to those described above for the joints aged at 150 °C.

A quantitative analysis of the thickness of the IMCs formed at the interface as a function of the aging time was performed. The thickness of the reaction layer in the solder joint can be generally expressed by the following simple power law equation:

$$W = kt^{1/2} + A$$

where W is the thickness of the IMC layer, k is the growth rate constant, t is the aging time and A is the thickness at $t = 0$.

Figs. 2 and 3 show the thicknesses of the IMC layers formed at the Sn–3.0Ag–0.5Cu/Cu and Sn–3.0Ag–1.0Cu/Cu interfaces as a function of the square root of the aging time, respectively. The thickness of the IMC layers was found to increase linearly with the square root of the aging time, and this dependence on $t^{1/2}$ indicates that the rate controlling mechanism for the growth of the IMC layers is a diffusion process [14]. The growth rate constant was calculated from a linear regression analysis of W vs. $t^{1/2}$, where the slope = k. The growth rate constants for the IMC layers formed at the interfaces are listed in Figs. 2(d) and 3(d), respectively. The growth rate constants for the IMC layers increased with increasing aging temperature.

The most interesting feature in Figs. 2 and 3 is that the addition of more Cu to the Sn–Ag solder significantly reduced the thickness of the Cu_3Sn IMC, while increasing the thickness of the total Cu–Sn and Cu_6Sn_5 IMCs. Compared to the Sn–3.0Ag–0.5Cu/Cu joint in Fig. 2(c), the growth of the Cu_3Sn layer is significantly depressed for the Sn–3.0Ag–1.0Cu/Cu joint in Fig. 3(c). In other words, the growth of the Cu_3Sn IMC became much slower when more Cu was added to the solder. On the other hand, the addition of more Cu to the solder had the effect of substantially increasing the amount of Cu_6Sn_5 IMC at the interface, as shown in Figs. 2(b) and 3(b).

It is interesting to note that the growth rate constants for the Cu_3Sn IMC of the Sn–3.0Ag–0.5Cu/Cu joint were higher than those of the Cu_6Sn_5 IMC at the aging temperatures of 150 and 170 °C, as shown in Fig. 2(d). On the other hand, the Cu_3Sn IMC grew slowly at relatively low aging temperatures of 100 and 120 °C, as shown in Figs. 2(c) and 3(c).

In comparing the two kinds of Sn–Ag–xCu/Cu solder joints investigated in this study, the most interesting aspect of the aged Sn–3.0Ag–1.0Cu/Cu joints was that the growth of the Cu_3Sn IMC was significantly retarded by the formation of the thick Cu_6Sn_5 IMC layer, due to the presence of more Cu in the solder, in comparison with the Sn–3.0Ag–0.5Cu/Cu system. Fig. 4 shows a comparison of the thickness of the IMC layers formed at the Sn–3.0Ag–0.5Cu/Cu and Sn–3.0Ag–1.0Cu/Cu interfaces aged at 150 °C. The Cu_3Sn IMC layer in the Sn–3.0Ag–0.5Cu/Cu joint was consistently thicker than that of the Sn–3.0Ag–1.0Cu/Cu joints after

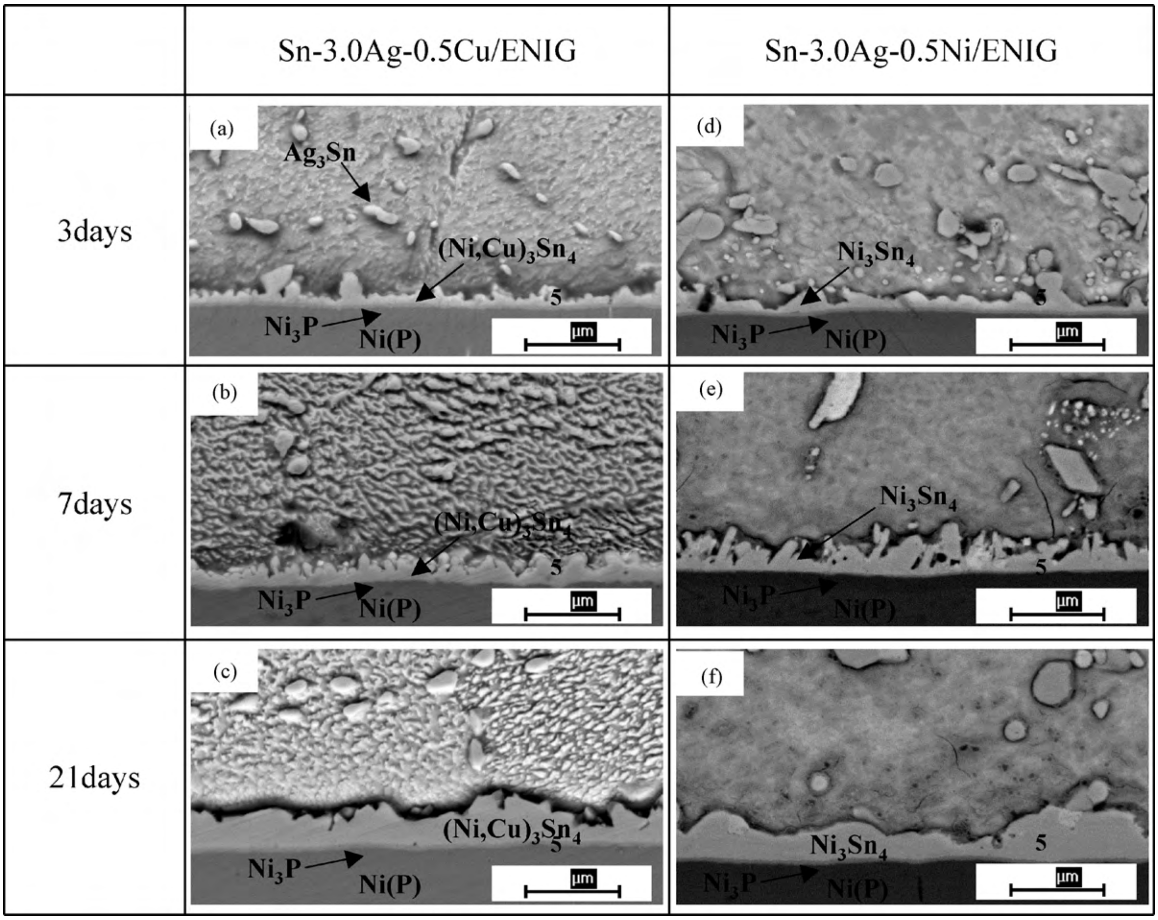


Fig. 5. Cross-sectional SEM images of the (a–c) Sn–3.0Ag–0.5Cu/ENIG and (d–f) Sn–3.0Ag–0.5Ni/ENIG interfaces aged at 150 °C for various times.

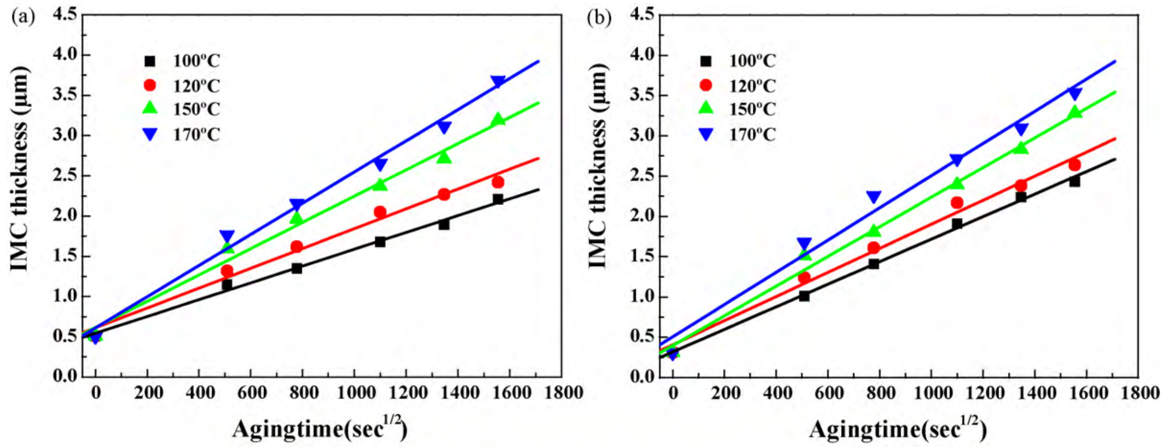
aging, as shown in Fig. 4(a). The proportion of Cu_6Sn_5–Cu_3Sn in the Sn–3.0Ag–0.5Cu/Cu joint after aging at 150 °C for 28 days is about 6–4. On the other hand, a Cu_6Sn_5/Cu_3Sn ratio of about 7:3 was observed in the Sn–3.0Ag–1.0Cu/Cu joint (Fig. 4(b)). This suggests that the addition of more Cu to the Sn–Ag solder effectively suppresses the growth of the Cu_3Sn IMC, while substantially increasing the amount of Cu_6Sn_5 IMC at the interface. In terms of total IMC thickness, the Sn–Ag–Cu solders containing less Cu would have a higher reliability and interfacial stability. On the other hand, Kirkendall voids would be more serious as the Cu_3Sn layer thickens [15]. The Kirkendall voids would result the decrease in the solder joint reliability. Therefore, we should consider both the total interfacial IMC thickness and the formation of Kirkendall voids for reliability of the Sn–Ag–Cu/Cu solder joint.

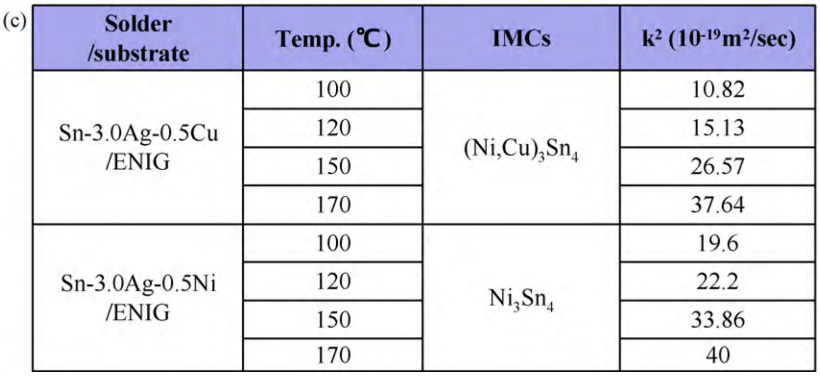
3.2. Sn–3.0Ag–0.5Cu/ENIG vs. Sn–3.0Ag–0.5Ni/ENIG

The formation and growth of the interfacial IMCs between the Ni-containing Sn–Ag–Ni solder and ENIG substrate were studied and the results were compared to those obtained for the Sn–Ag–Cu/ENIG system. Fig. 5(a)–(c) shows the cross-sectional SEM images of the Sn–3.0Ag–0.5Cu/ENIG interfaces aged at 150 °C for different aging times. In the as-reflowed condition, the entire Au layer on the Ni(P) layer dissolved into the molten solder and the Sn–Ag–Cu solder formed only an $(Ni,Cu)_3Sn_4$ IMC at the solder/Ni(P) interface. During reflow, the Sn and Cu atoms in the solder arrived at the solder/Ni(P) interface, causing the formation of the Cu-containing $(Ni,Cu)_3Sn_4$ IMC. Therefore, even though the Cu content in the solder is very low (0.5 wt.%), the formation of the $(Ni,Cu)_3Sn_4$ IMC is dependent on the reaction of Cu, Sn and Ni in the Sn–Ag–Cu/Ni(P) solder joint. The thickness of the $(Ni,Cu)_3Sn_4$ IMC layer is found to increase with increasing aging time. Even when the aging time was prolonged up to 21 days, only the $(Ni,Cu)_3Sn_4$ IMC layer was observed at the Sn–Ag–Cu/ENIG interface, as shown in Fig. 5(c).

Fig. 5(d)–(f) shows the cross-sectional SEM images of the Sn–3.0Ag–0.5Ni/ENIG interfaces aged at 150 °C for different aging times. Only Ni_3Sn_4 IMC formed at the Sn–Ag–Ni/ENIG interface and its thickness increased with increasing aging time. The thicknesses of the IMC layers formed at the Sn–3.0Ag–0.5Cu/ENIG and Sn–3.0Ag–0.5Ni/ENIG interfaces as a function of the square root of the aging time and the calculated growth rate constants are shown in Fig. 6. When comparing the two kinds of solder joints (Sn–Ag–Cu/ENIG and Sn–Ag–Ni/ENIG), no significant difference was observed and their interfacial microstructures were found to be a similar, as shown in Figs. 5 and 6, respectively.

Lastly, we compared the IMC thickness of the four kinds of Sn–Ag–Cu(or Ni)/Cu(or ENIG) solder joints investigated in this study. Fig. 7 shows the thickness of the IMC layers formed at the interfaces of the solder joints aged at 150 °C. The IMC growth of the Sn–3.0Ag–1.0Cu/Cu joint was the fastest. Comparing the Sn–3.0Ag–0.5Cu/Cu and Sn–3.0Ag–0.5Cu/ENIG solder joints, the growth rate constant ($86.44 \times 10^{-19}\,m^2/s$) for the Cu substrate was about 3.3 times faster than that for the ENIG substrate ($26.57 \times 10^{-19}\,m^2/s$). As a result, the interfacial reaction on the Cu substrate was much faster than that on the ENIG substrate. The results of this study clearly demonstrate the advantages of the ENIG substrate and the use of a solder containing less Cu, in order to ensure the high temperature reliability and interfacial stability of Sn–Ag–Cu (or Ni) solder joints from the total IMC thickness aspect.





(c)

Solder /substrate	Temp. (℃)	IMCs	k^2 (10^{-19} m^2/sec)
Sn-3.0Ag-0.5Cu /ENIG	100	$(Ni,Cu)_3Sn_4$	10.82
	120		15.13
	150		26.57
	170		37.64
Sn-3.0Ag-0.5Ni /ENIG	100	Ni_3Sn_4	19.6
	120		22.2
	150		33.86
	170		40

Fig. 6. Thickness of the IMC layers formed at the (a) Sn–3.0Ag–0.5Cu/ENIG and (b) Sn–3.0Ag–0.5Ni/ENIG interfaces during isothermal aging, and (c) calculated growth rate constants.

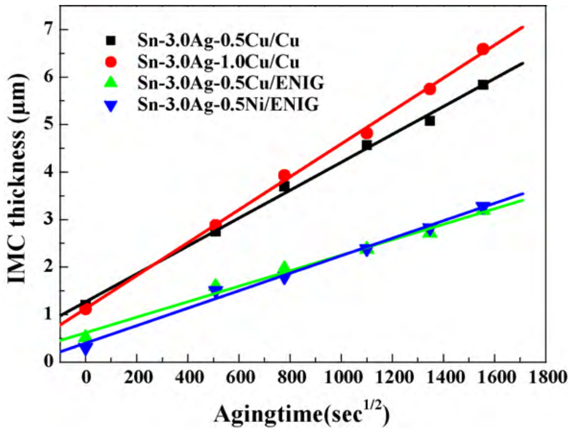


Fig. 7. Thickness of the IMC layers formed at the interfaces of solder joints aged at 150 °C.

4. Conclusion

We investigated the effects of a third element (Cu or Ni) and substrate type (Cu or ENIG) on the interfacial reactions of Sn–Ag–*x*Cu (or Ni)/Cu (or ENIG) solder joints. The following conclusions were reached.

- In the solid-state reactions of the Sn–Ag–*x*Cu/Cu solder joints, the two IMC layers, Cu_6Sn_5 and Cu_3Sn, grew with increasing aging temperature and time. The addition of more Cu to the Sn–Ag solder significantly reduced the thickness of the Cu_3Sn IMC, while increasing the thickness of the total Cu–Sn and Cu_6Sn_5 IMCs. The growth of the Cu_3Sn IMC in the Sn–3.0Ag–1.0Cu/Cu joints was significantly retarded by the formation of the thick Cu_6Sn_5 IMC layer, due to the presence of more Cu in the solder, in comparison with the Sn–3.0Ag–0.5Cu/Cu system.
- In the case of the Sn–3.0Ag–0.5Cu/ENIG joint, $(Ni,Cu)_3Sn_4$ IMC formed and grew at the interface during isothermal aging. On the other hand, only Ni_3Sn_4 IMC formed at the Sn–3.0Ag–0.5Ni/ENIG interface. When comparing the Sn–Ag–Cu/ENIG and Sn–Ag–Ni/ENIG solder joints, no significant difference was observed and the interfacial microstructure was found to be similar.
- Comparing the Sn–3.0Ag–0.5Cu/Cu and Sn–3.0Ag–0.5Cu/ENIG solder joints, the growth rate of the IMC layer for the Cu substrate was about 3.3 times faster than that for the ENIG substrate. As a result, the interfacial reaction on the Cu substrate was much faster than that on the ENIG substrate.

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