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EFFECT OF Co ADDITION ON INTERFACE REACTION BETWEEN Sn–Ag–Cu SOLDER AND Cu SUBSTRATE

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Sn−Ag−Cu (SAC) alloys are considered as the most promising Pb-free solders in electronic industry. The solidification microstructure and interface reaction behaviors of SAC alloys are therefore of fundamental importance for the service reliability of electronic devices. This is particularly true for these SAC alloys with low silver contents, partially because the coarsened interfacial intermetallics (IMCs) of these low-Ag SAC alloys with higher surface tension than conventional near-eutectic SAC alloys. As a result, it is desirable to refine the grain size of interfacial IMCs between low-Ag alloys and common substrates such as Cu. In this work, the effects of addition of trace amount of Co on the interface reaction between both conventional SAC305 and low-Ag SAC107 alloys on Cu substrate have been studied by reflowing experiments at temperature close to 260 °C. In addition, effects of Co additions on the solid state growth of interfacial IMCs have been studied at 150 °C after ultra-long annealing treatment for 384h, 768, and 1536h. Both top-view and cross-section micro-graphs have been obtained using electron microscopes. It has been found that addition of trace amount of Co can significantly refine the interfacial Cu_6Sn_5 IMCs grains after reflow process and impede the growth of Cu_3Sn after annealing treatment. This attributed to the replacement of Cu atoms by Co atoms in Cu_6Sn_5 crystals, which in turn depresses the diffusion of Cu and impedes the transformation from Cu_6Sn_5 to Cu_3Sn during aging.

Keywords: lead-free solder, Sn−Ag−Cu, intermetallic compound, microstructure

Sn−Ag−Cu (SAC) alloys are considered as the most promising Pb-free solders in electronic industry. In order to further reduce the cost of SAC solder, new SAC alloys with lower Ag content have been widely studied [1], and alloying elements, such as Ni, Bi, Co, are selected as additions into these alloys [2−4]. In particular, the addition of trace amount of Co can effectively reduce the undercooling of Sn−Ag−Cu solder alloys, improve the mechanical properties, retard the formation of Cu3Sn IMCs, and suppress the void formation during interfacial reactions with Cu substrate [5−7].

In this work, the effects of addition of trace amount of Co on the interface reaction between both conventional SAC305 and low-Ag SAC107 alloys on Cu substrate have been studied by reflowing experiments at temperature close to 260 °C. In addition, effects of Co additions on the solid state growth of interfacial IMCs have been studied at 150 °C after ultra-long annealing treatment for 384h, 768, and 1536h. Both top-view and cross-section micro-graphs have been obtained using electron microscopes.

Experimental. Sn−3.0Ag−0.5Cu−*x*Co (*x* = 0, and 0.2 wt.%) and Sn−1.0Ag−0.7Cu−*x*Co (*x* = 0, and 0.07 wt.%) alloys were prepared, and then reflowed on Cu substrate using a RMA flux. The maximum soldering temperatures for Sn−3.0Ag−0.5Cu−*x*Co and Sn−1.0Ag−0.7Cu−*x*Co alloys were 260 °C and 265 °C, respectively, and the samples were cooled in the air after reflowing for 30 seconds. To reveal the effects of Co additions on the interface morphology of IMCs, microstructure observation was performed using an optical microscopy (VHX-900) and electron microscopy (JSM 6480).

Results and discussion. The cross-sections of IMC layers at solder/Cu interface in the as-sol-

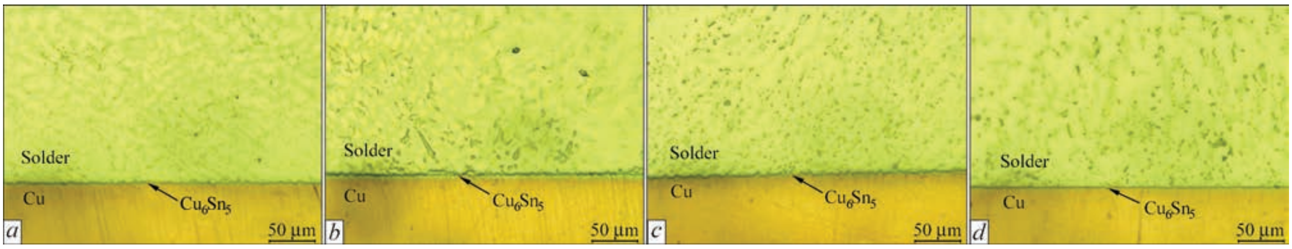

Figure 1. Cross-sections of IMC layer in as-soldered samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

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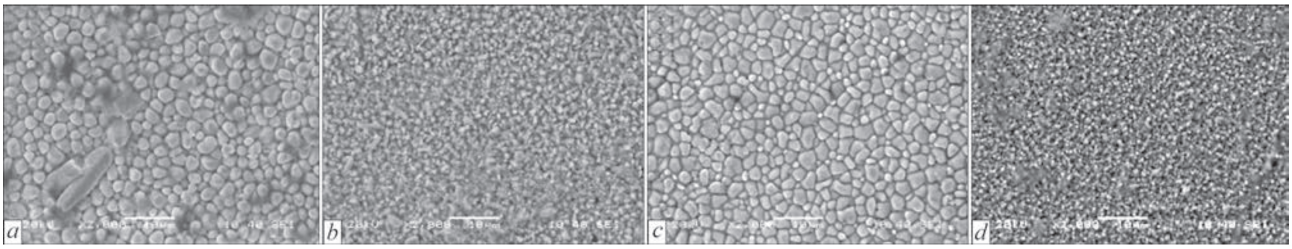

Figure 2. Top-views of IMC layer in as-soldered samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

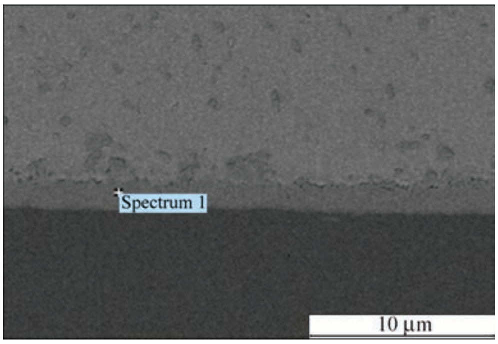

Figure 3. EDX test of IMC layer in as-soldered Sn−1.0Ag−0.7Cu−0.07Co sample

dered samples are shown in Figure 1. The morphologies of Cu_6Sn_5 are scallop-like in the as-soldered Sn−3.0Ag−0.5Cu and Sn−1.0Ag−0.7Cu samples (Figure 1, *a*, *c*), and thicker interfacial IMCs can be observed in the other two samples.

In the top-views as shown in Figure 2, it is found that the morphology of interfacial IMC is round shape in all the as-soldered samples after deep etching, while the sizes of interfacial IMCs grains with Co addition are much smaller than those of without Co addition. In other words, the addition of trace amount of Co can significantly refine the interfacial Cu_6Sn_5 IMCs grains after reflow process.

Table 1 shows the EDX results of interfacial IMC layers in as-soldered Sn−3.0Ag−0.5Cu−0.2Co and Sn−1.0Ag−0.7Cu−0.07Co samples in Figures 2, 3, in order to determine the composition of the interfacial IMC layer between the Sn−Ag−Cu−Co solder and Cu substrate. The intermetallic phase is likely to be expressed as $(Cu, Co)_6Sn_5$ phase, which is considered to be formed by substituting Cu atoms in binary compounds by Co atoms, consistent with previous result reported by Nishikawa et al. [7].

The morphologies of IMCs layer at the interface change obviously after isothermal aging, and severe coarsening and planarization of IMC grains can be found. The morphologies of Cu_6Sn_5 in Sn−3.0Ag−0.5Cu and Sn−1.0Ag−0.7Cu samples are planarized to be a thick layer after isothermal aging, while the interfacial IMC are much thicker with addition of trace amount of Co, as the cross-sections of the interface aged at 423 K for 384h in Figure 4. In the top-views of the IMC layers as shown in Figure 5, the morphologies of interfacial IMC are changed from roundshape into polyhedron-shape after isothermal aging. The grain sizes of interfacial IMC with Co addition are still smaller, and the grain refinement effect is obtained with 0.2 % Co addition.

After aged for 768h and 1536h, the Cu_3Sn layer can be obtained obviously at the cross-sections of the interface between SAC alloys and Cu substrates as shown in Figure 6, 8, which decreases the mechanical strength of solder joint due to its brittleness nature and

Table 1. EDX results of interfacial IMC layers in as-soldered samples

Region	Solder	Element, at.%		
		Sn	Cu	Co
Cross-section in Figure 3	SAC107−0.07Co	46.68	50.45	2.87
Top-view in Figure 2	SAC305−0.2Co	44.75	47.13	8.12
Top-view in Figure 2	SAC107−0.07Co	43.06	53.90	3.04

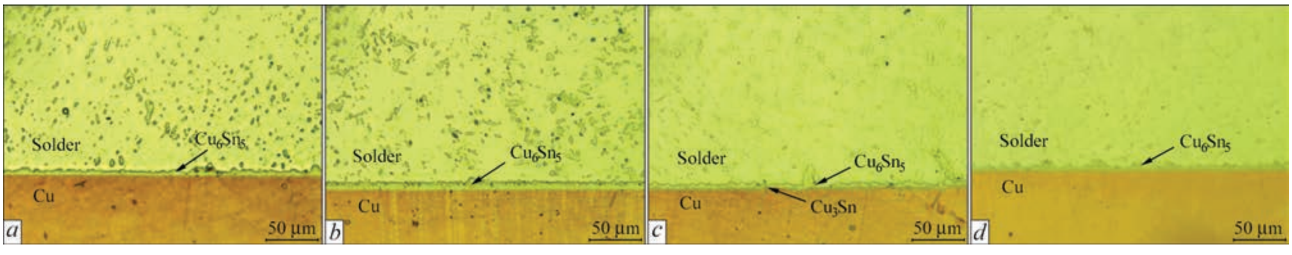

Figure 4. Cross-sections of IMC layer in 384h aged samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

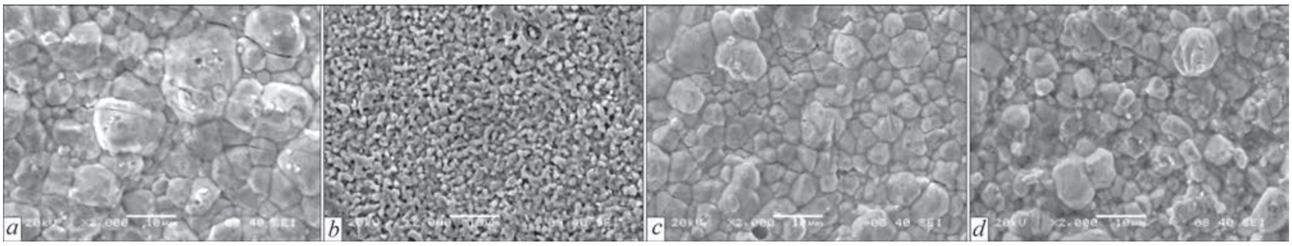

Figure 5. Top-views of IMC layer in 384h samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

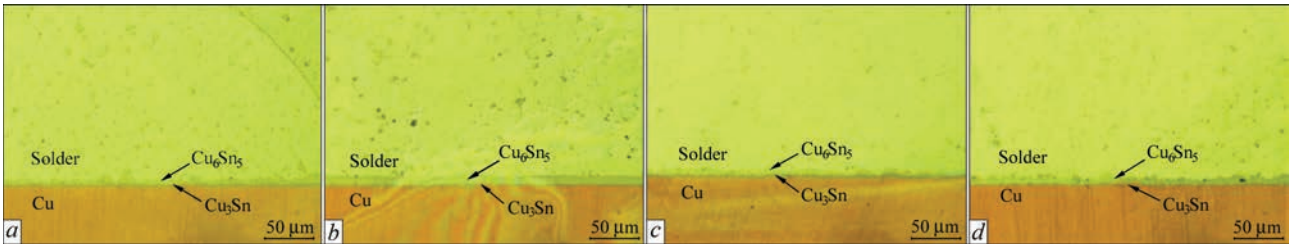

Figure 6. Cross-sections of IMC layer in 768h aged samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

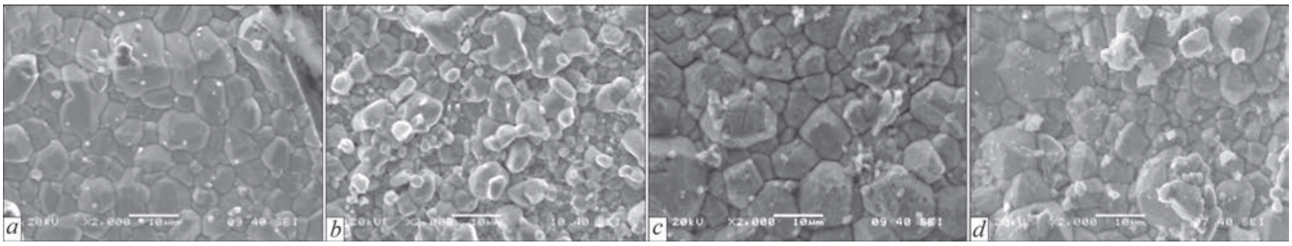

Figure 7. Top-views of IMC layer in 768h samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

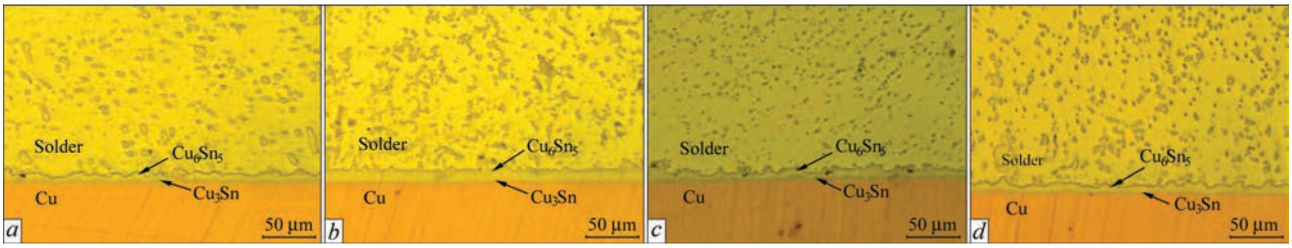

Figure 8. Cross-sections of IMC layer in 1536h aged samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

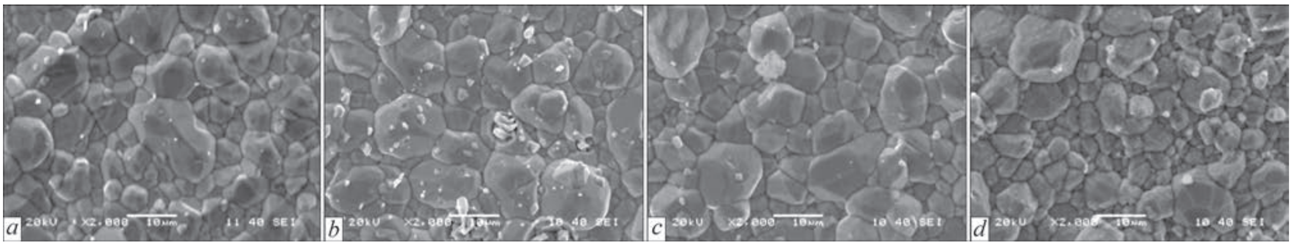

Figure 9. Top-views of IMC layer in 1536h samples: *a* — Sn−3.0Ag−0.5Cu; *b* — Sn−3.0Ag−0.5Cu−0.2Co; *c* — Sn−1.0Ag−0.7Cu; *d* — Sn−1.0Ag−0.7Cu−0.07Co

different CTE [8]. It is found that addition of trace amount of Co can impede the growth of Cu_3Sn after aging treatment, attributed to the replacement of Cu atoms by Co atoms in Cu_6Sn_5 crystals, which in turn depresses the diffusion of Cu and inhibits the transformation from Cu_6Sn_5 to Cu_3Sn during thermal aging. At the same time, the grain refinement effect of Co addition becomes weaker as the aging time increasing, and the sizes of interfacial IMC grains in all samples become the same after 768h aging, according to the top-views in Figures 7, 9.

Conclusions

- Trace amount of Co can significantly refine the interfacial Cu_6Sn_5 IMCs grains after soldering.
- Co can inhibit the growth of Cu_3Sn after annealing treatment.
- Cu atoms are replaced by Co atoms in Cu_6Sn_5 crystals, depressesing the diffusion of Cu and impeding the transformation from Cu_6Sn_5 to Cu_3Sn during aging.

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