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Intermetallic compounds evolution between lead-free solder and cu-based lead frame alloys during isothermal aging

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This paper investigated the intermetallic compounds (IMCs) formation between SnAgCu solder and four Cu-based lead frame alloys during reflow soldering and isothermal aging. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) were used to study the cross-sectional microstructure and stoichiometric information. Optical Microscope (OM) was used to measure the mean thickness of IMCs. It was found that Ni and Sn trace element have important influences on the interfacial reactions. After soldering, for the case of Sn-Ag-Cu solder on Cu-Sn-Cr-Zn, Cu-Sn-P and Cu-Fe-P-Zn-Pb, an island type Cu6Sn5 and a thin Cu3Sn layer were formed at the interface. However, for the case on Cu-Ni-Si-Mg alloy, no Cu3Sn was detected and only a layer of ternary (Cu,Ni)6Sn5 was confirmed and some Cu6Sn5 particles was observed to disperse in the bulk solder. The top morphology of IMCs was also characterized after the solder was selectively etched away. The IMCs on the Cu-Ni-Si-Mg showed long rod-like shape, whilst the IMCs on the other three alloys appeared round. After different duration of aging at 150°C, all the IMCs grew thicker and the grain size became larger. The rod-like IMCs on Cu-Ni-Si-Mg gradually transformed into round shape and it was relatively smaller compared to that on the other three alloys. Moreover, the growth rate of IMCs on Cu-Ni-Si-Mg is the fastest among the four alloys. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Lead frame is widely used in electronics packaging. Due to excellent thermal and electrical properties plus low cost, Cu-based alloys have been employed as the most popular lead frame material. During soldering process, the interfacial reaction happens between the package leads and liquid solder. Metallurgical bond is created by the formation of Intermetallic Compounds (IMCs) at the interface. In one hand a continuous layer of IMCs is absolutely necessary for package integrity, while on the other hand IMCs are the brittle parts of the solder joint, thus raising reliability concerns for long term application.

SnPb solders have been employed in electronic manufacturing industry for a long time. However, due to environmental concerns and legislation limitations, removal of Pb is an ongoing effort of many manufacturers around the world. By years of extensive investigations, SnAgCu alloy has been developed as the most promising lead-free solder [1–4]. RoHS has demanded elimination of lead from electronics products by July 1, 2006. Many world

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famous companies are already making mass with lead-free process. Because SnAgCu solder has higher melting temperature (about 217°C) than SnPb solder (183°C), interfacial reaction will occur under a higher temperature and IMCs will grow thicker than the case for SnPb solder. The fact that component, solder paste and PCB may use different lead-free solutions raise very complex compatibility issue. The unavoidable lead-free transition on timing further complicates the case by carrying forward compatibility and backward compatibility. Another point worthy to mention is fast growing mobile application, in which mechanical stresses appear as one major challenge. Evidently, the thicker IMCs in lead-free case are susceptible for arising such stresses than the case for SnPb.

Many studies on interfacial reactions between SnAgCu solder and metallizaitons have been reported [5–8]. The effects of IMCs formation on mechanical properties and reliability of solder joints under different experimental conditions were also studied [9–13]. Hua *et al.* [14] investigated adhesive strength of Cu-based lead frame and Alloy 42 soldered with Pb-containing solder under isothermal aging. They found that Cu-based lead frame had better adhesive strength than Alloy 42 and the IMCs had important influences on the adhesive strength. We know that some trace elements, such as Sn, Cr, Zn, P, Si, Mg, Ni, Fe, Pb, are selectively added into the Cu to obtain desired manufacturability and mechanical properties in industry. Huang *et al.* [15] studied the effect of chemical composition of Cu alloys on interfacial reaction between Cu alloys and SnPb solder. Two Cu-based alloys with different trace elements were soldered to SnPb solder and subsequently aged at 160°C. Microstructure evolution and growth rate of IMCs was compared. But they didn't clearly discuss the effects of trace element on IMCs formation. No systematic works have been reported on interfacial reaction between lead-free solder and lead frame materials. In this paper, we investigate the compositional effects of Cu-based lead frame materials on the IMCs growth and microstructure evolution during soldering and isothermal aging.

2. Experimental procedure

The compositional information of four Cu-based alloys from Mitsui High-Tec (Shanghai) Co., Ltd. are confirmed by X-Ray Fluorescence (XRF) and listed in Table I. For convenience, the alloys are marked as A, B, C, D. The alloys are cut into 5 mm × 5 mm sheet substrates and polished for joining with the solders. Commercial Sn-3.0Ag-0.5Cu solder paste were printed on the Cu-based substrates and then reflowed in a full air convection oven to prepare solder joints. The peak temperature of reflow profile and dwell time above liquidus temperature (217°C in this case) was 250°C and 120 seconds, respectively. After soldering, the specimens were isothermally aged at 150°C for different duration up to 300 hours. Samples were mounted, cross-sectioned and polished to study the solder/alloy interfaces. Optical microscope and SEM were used to characterize interfacial microstructure of the solder joint. The mean thickness of the IMCs was an average of fifteen measurements at different locations. In EDX detection, three points were taken into account for the analysis of each element. For some samples, the solders were chemically etched in dilute HNO3 acid solution with the aid of ultrasonic to observe the morphology of IMCs.

TABLE I Composition of Cu-based lead frame alloys

Sample	Alloy name	Chemical composition (wt%)
A	EFTEC64T	Cu-0.26Cr-0.24Sn-0.2Zn
B	C5191	Cu-5.5Sn-0.05P
C	C7025	Cu-2.2Ni-0.55Si-0.06Mg
D	C194ESH	Cu-2.2Fe-0.08P-0.07Zn-0.03Pb

3. Results and discussions

3.1. Interfacial microstructures

The interfacial microstructures of soder/alloys after soldering were shown in Fig. 1. For the case of Sn-Ag-Cu on alloy A, B and D, as shown in Fig. 1a, (b) and (d), one thick layer of irregular island-type IMCs is observed at interfaces. Also a very thin darker layer which is indiscernible under SEM formed adjacent to Cu. EDX analysis confirmed the thick IMC layer was Cu6Sn5 and the thin layer was Cu3Sn. For the case of Sn-Ag-Cu on alloy C, as shown in Fig. 1c, only one layer of IMC is observed at the interface, more planarized than the other three cases. However, adjacent to the interface, rod-like particles are found dispersed into the bulk solder. The dispersed IMC was confirmed to be Cu6Sn5 by EDX. The planar layer was detected to be approximate (Cu,Ni)6Sn5, in which the Ni concentration varied from 2 to 4 atomic percent. Obviously the Cu in the Cu6Sn5 was partially replaced by some Ni from lead frame to form (Cu,Ni)6Sn5 solid solution. Contrary to the case of alloy A, B and D, no Cu3Sn layer is detected at the interface.

Fig. 2a–d showed cross-sectional SEM images of solder/alloy interfaces after aging at 150°C for 300h. For the case of alloy A, B and D, the IMCs layers grew thicker and tended to planarize. Cu3Sn at the interface of alloy B reveals much thicker than alloy A and D. In Fig. 2c, the rod-like grains grew longer, wider and faster than those in the case of A, B and D, and again no Cu3Sn exists.

3.2. Top morphology of IMCs grain

Fig. 3 showed the top morphology of IMCs after reflow soldering. After reflow soldering, for the case of alloy A, B and D, as shown in Fig. 3a, b and d, the IMC reveals round grains. The grain size of case A and B is both about 8 μm, which is greater than 6 μm of the case D. The IMCs on the alloy C, as shown in Fig. 3c, appears distinct rod-like morphology. As aging, IMCs grains got coarsening and kept round morphology for the case A, B and D. For the

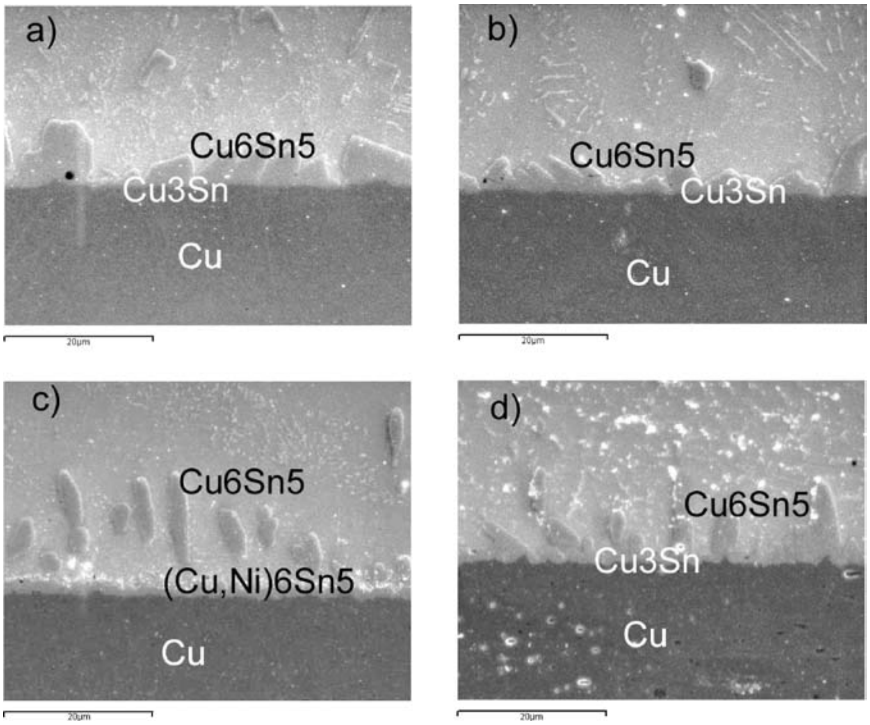

Figure 1 Cross-sectional SEM images of the as-reflowed samples: (a)–(d) was interface of sample A-D, respectively.

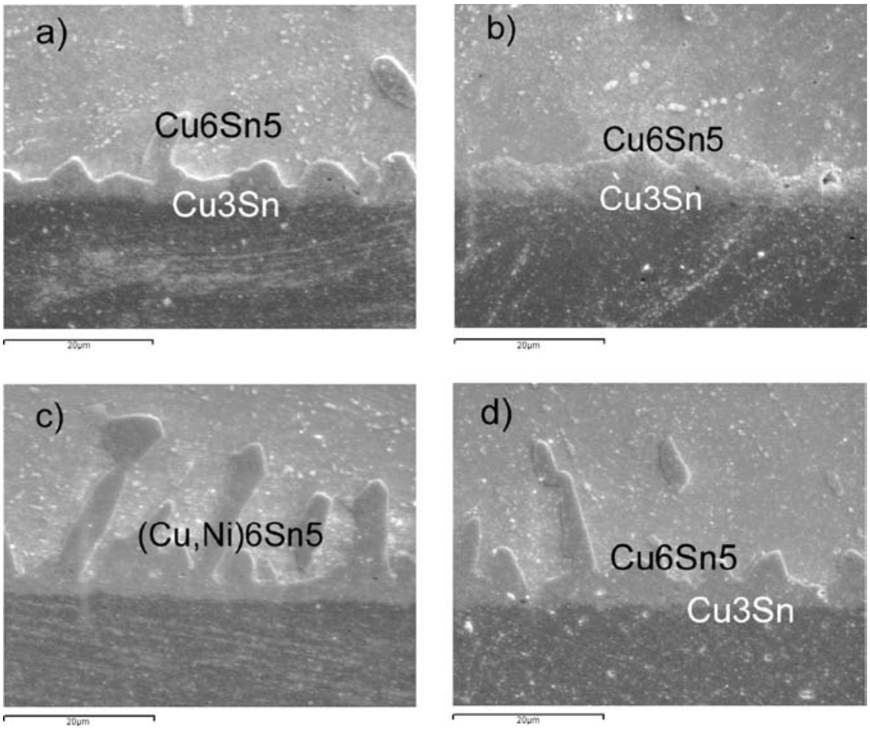

Figure 2 Cross-sectional SEM images of the samples after aging at 150°C for 300 hours: (a)–(d) was interface of sample A-D, respectively.

case of alloy C, round and rod-like grains coexisted after 10 hours of aging, as shown in Fig. 4c. After 300 hours of aging, it was found that the morphology of IMCs changed to round and grain size is much smaller than those of the other three cases.

3.3. IMCs growth kinetics

The kinetics of IMCs growth can be diffusion controlled or interfacial-reaction controlled [16–18]. Fig. 6a plotted the mean thickness of total IMCs in each case after different aging time. The curves indicates that the IMCs growth

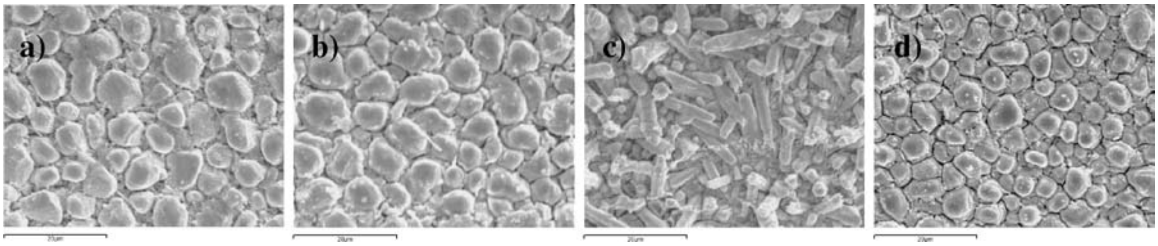

Figure 3 Top morphology of IMCs of four Cu-based alloys as-reflowed: (a)–(d) was the case of alloy A-D, respectively.

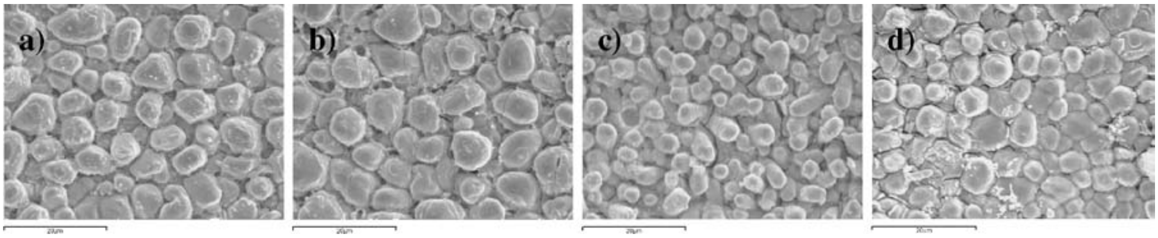

Figure 4 Top morphology of IMCs of four Cu-based alloys after 10 hours of aging: (a)–(d) was the case of alloy A-D, respectively.

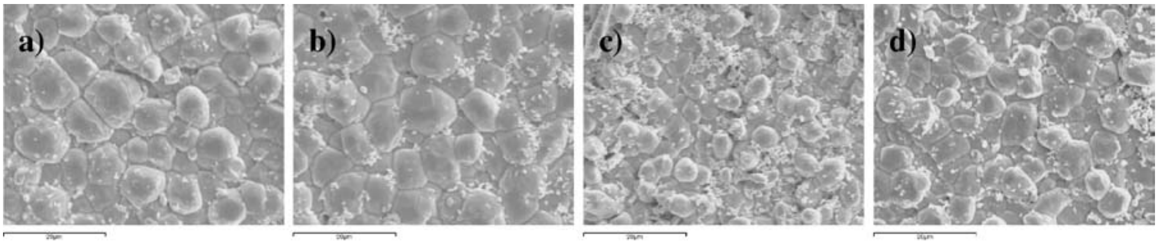

Figure 5 Top morphology of IMCs of four Cu-based alloys after 300 hours of aging: (a)–(d) was the case of alloy A-D, respectively.

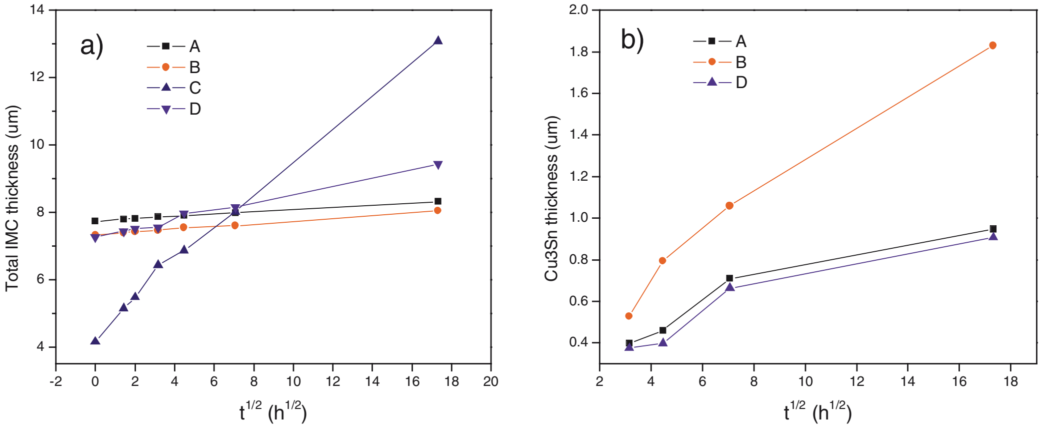

Figure 6 Mean thickness of IMCs layers versus isothermal aging time: (a) thickness of total IMCs; (b) thickness of Cu3Sn.

is corresponded with diffusion-controlled, which can be expressed as the following empirical equation:

$$X(t) - X_0 = \sqrt{Dt} \tag{1}$$

Where $X(t)$ is the IMCs thickness at aging time t, X_0 is the initial thickness after soldering and D is the solid diffusion coefficient.

From Fig. 6a, IMCs formed in alloy C is much thinner than that in other three cases after reflow soldering. During isothermal aging, the thickness of IMCs in alloy C is the smallest among the four cases until aging 50 hours. After aging for 300 hours, IMCs in alloy C grew much thicker than the other cases. Korhonen *et al.* [19, 20] found that even small Ni addition to Cu would slow down the dissolution of Cu into molten solder and the formation of IMCs during liquid reaction. In our research, the thickness of IMCs revealed simlilar results. The formation of IMCs in containing Ni trace element (alloy C) was suppressed in reflow soldering. However, the reaction rate in the case

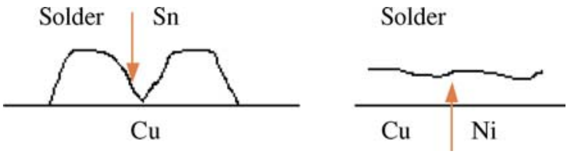

Figure 7 Schematic diagram of interfacial reaction.

of alloy C is the fastest during solid state reaction. D in Equation 1 can represent Cu consumption rate and interfacial reaction velocity in some extent. The D value was calculated to be $3.047 \times 10^{-15} \text{cm}^2/\text{s}$, $4.604 \times 10^{-15} \text{cm}^2/\text{s}$, $6.986 \times 10^{-13} \text{ cm}^2/\text{s}$ and $4.388 \times 10^{-14} \text{cm}^2/\text{s}$ for the case of alloy A, B, C, D, respectively. The D value for the case of alloy C is one to two orders of magnitude greater than other cases. Fig. 6b plotted the mean thickness of Cu3Sn with aging time. For the case of alloy B, the thickness of Cu3Sn increased very fast compared to the case of alloy A and D, which had nearly equal thickness.

3.4. IMCs formation mechanism

A schematic diagram shown in Fig. 7 can be used to explain difference in interfacial microstructures of four Cu-based alloys. During reflow soldering Cu-Sn reaction occurred and formed a layer of IMCs, which in turn blocked the atoms diffusion and inhibited further interfacial liquid/solid reaction. For alloy A, B and D, typical island IMCs layers formed at solder/Cu interfaces. A solid-state diffusion through the bulk of Cu6Sn5 was a slow kinetic process. Cu would diffuse through the valleys between island grains fast to reach the solder/Cu6Sn5 interface, that Cu-Sn reaction proceeded and Cu6Sn5 grew thicker. For the case of alloy C, the IMCs layer revealed rather planar after reflow soldering. However, ternary (Cu,Ni)6Sn5 grew faster than binary CuSn IMCs during solid state reaction. The thickness of IMCs on alloy C became thicker than others cases after about 50 hours aging (Fig. 6a). This result agrees with the observations reported by Chang [21]. Chang investigated IMCs evolution at Ni/SnAgCu and Cu/SnAgCu interfaces under thermal shock. The growth rate of ternary IMCs at Ni/SnAgCu interface is faster than that of Cu-Sn IMCs at Cu/SnAgCu interface.

IMCs layer has a planarization tendency during isothermal aging. Choi *et al.* [22] suggested that the morphology transition was due to the reduction in surface-free energy. Island IMCs had larger surface area than a planar layer of similar thickness, resulting in a large driving force for surface energy change. Deng *et al.* [23] attributed the planarization process to the shorter diffusion distance between island valleys and Cu substrate, when compared to the distance between island peak and Cu substrate. Thus Cu diffused faster to the island valley than to the island peak, leading to faster growth rate at the valley and subsequent planarization of the whole IMCs layer.

Cu will react with Cu6Sn5 to form Cu3Sn phase at Cu6Sn5/Cu interface [23–25]. Cu3Sn grows thicker at the expense of part of existing Cu6Sn5. But in the case of alloy C no Cu3Sn phase was detected even after 300 hours aging. Previous studies also reported [26, 27] that Cu3Sn phase was retarded at the presence of Ni, the reason is not clear yet. The Ni trace element in the Cu-based alloy plays a crucial influence on the formation of IMCs at interface. Prakash *et al.* [25] found that Sn concentration at Cu6Sn5/Cu interface must reach a definite value before Cu3Sn phase grows to detectable levels. This leads to an incubation time for Cu3Sn phase growth. From Fig. 6b we can observe that the Cu3Sn layer is the thickest in the case of alloy B which contains higher Sn concentration (5.5 wt%) and the incubation time is shorter. Alloy A contains a few Sn (0.24%), the thickness of Cu3Sn in the case A is much smaller than that of case B. And for the case of alloy D Cu3Sn is a little smaller than that of case A. Whether this is a several correlation or not leads more investigation.

4. Conclusion

The IMCs evolution between Sn-Ag-Cu solder and four Cu-based lead frame alloys were compared and it was found that Ni and Sn trace element have important influences on the interfacial reactions during the soldering and solid state aging.

- With additive Ni trace elment into Cu-based lead frame, instead of the formation of a typical island Cu6Sn5 layer and a thin Cu3Sn layer, a layer-type ternary (Cu,Ni)6Sn5 IMCs forms at the interface and no Cu3Sn phase is detected. The top morphology of ternary IMCs reveals distinct rod-like compared with rounded Cu6Sn5 IMCs.
- Ni element increases the growth rate of IMCs and the top morphology of IMCs gradually transforms from rod-like into round during isothermal aging. After aging 300 hours, the thickness of IMCs is much greater than the other cases and no Cu3Sn forms yet.
- Additive Sn element in Cu-based alloy promotes the growth of Cu3Sn phase. Since higher Sn concentration decreases the incubation time of the formation of Cu3Sn, thus facilitating growth of Cu3Sn.

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