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Effect of trace Al on growth rates of intermetallic compound layers between Sn-based solders and Cu substrate

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ABSTRACT

This paper reports the effect of the addition of 1 wt% Al into 100Sn, 96.5Sn–3.5Ag (SA) and 95.5Sn–3.8Ag–0.7Cu (SAC) solders, on growth rates of intermetallic compound (IMC) layers between the solders and a Cu substrate. During reflow at 260 °C under $2\%H_2 98\%N_2$ forming gas for 5–120 min, the most pronounced reduction in IMC growth was observed in the SAC–1Al/Cu system. This was accompanied with the evolution of a layer of η_2 (AlCu) IMC which was first formed within the bulk of the solder, then migrated towards and gradually replaced the previously formed η (Cu_6Sn_5) and ε (Cu_3Sn) IMCs at the solder/Cu interface, and was finally transformed into δ (Al_2Cu_3) IMC and dispersed into the bulk of the solder again. A similar reduction in growth and associated evolution of IMCs was observed in the SAC–1Al/Cu samples subjected to thermal ageing at 170 °C under air for 24–2096 h.

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1. Introduction

With higher levels of integration and increased power densities, electronic assemblies and systems are required to function reliably at elevated temperatures. In the various electronic assemblies and systems, near-eutectic Sn–Ag–Cu and Sn–Ag solders are widely used to attach semiconductor devices on supporting substrates for supplying thermal, electrical and mechanical connections [1–3]. However, the solder joints are generally weak points leading to failure of electronic assemblies and systems operated at temperatures above 125 °C [4]. This is because the solders are prone to creep at elevated temperatures and the accumulation of plastic work leads to crack initiation and propagation [3,5]. Rapid growth of intermetallic compounds (IMCs) between the solders and the contact metallizations on both the semiconductor devices and the supporting substrates may also take place, resulting in brittle fracture of the joints [2,6]. This is especially true when an electronic system is subjected to deep thermal cycling, vibration and/or shock loadings [7].

Several materials and processes under research and development may be used as potential alternatives to improve the reliability of solder joints in electronic assemblies and systems operated at elevated temperatures. These include transient liquid phase (TLP) soldering [8–10], sintering of Ag particles and nano-particles [11], nano-particle reinforced solders [12,13], emerging solder alloys [14,15], local brazing [16], and liquid solder joint [17]. Of these, powder-based TLP soldering [10], nano-particle reinforced solders and emerging solder alloys are more compatible with the conventional solder reflow process. The other materials and processes may have greater benefits, but require some modification of the conventional solder reflow process.

The motivation behind developing and using nano-particle reinforced solders and emerging solder alloys to improve reliability of solder joints are: (i) to refine the microstructure, slow down the growth of interface IMCs and (ii) improve the mechanical properties at elevated temperatures. For example, Co, Ni and Pt nano-particles added into Sn–Ag based solders were found to be effective in reducing the growth of IMCs between the solders and Cu contact metallization and to improve the drop test performance [12]. Addition of rare-earth (RE) Er into Sn–Ag–Cu solder may refine the microstructure of the solder matrix and eliminate crack nucleation and propagation of the solder joints on Cu during the aging process at 170 °C for 1000 h [15].

Cu is used extensively in lead-frames, lead-traces, contact metallization on printed circuit boards (PCBs) and increasingly as an interconnection layer on semiconductor devices [1,2]. There is a wealth of studies on the kinetics of IMC growth between solid Sn-based solders and various types of Cu contact metallizations under thermal ageing [2,5,18]. The IMCs formed during the soldering process also play an important role in the wettability of solders. Thus there are some studies of IMC formation between molten solders, including Sn–Ag–Cu, Sn–Pb, Sn–Ag, Sn–Sb, Sn–Zn, Sn–Bi and pure Sn, and various contact metallizations containing Cu [18–21]. Results from these studies show that the IMC growth rates in these solder/Cu systems are rather high.

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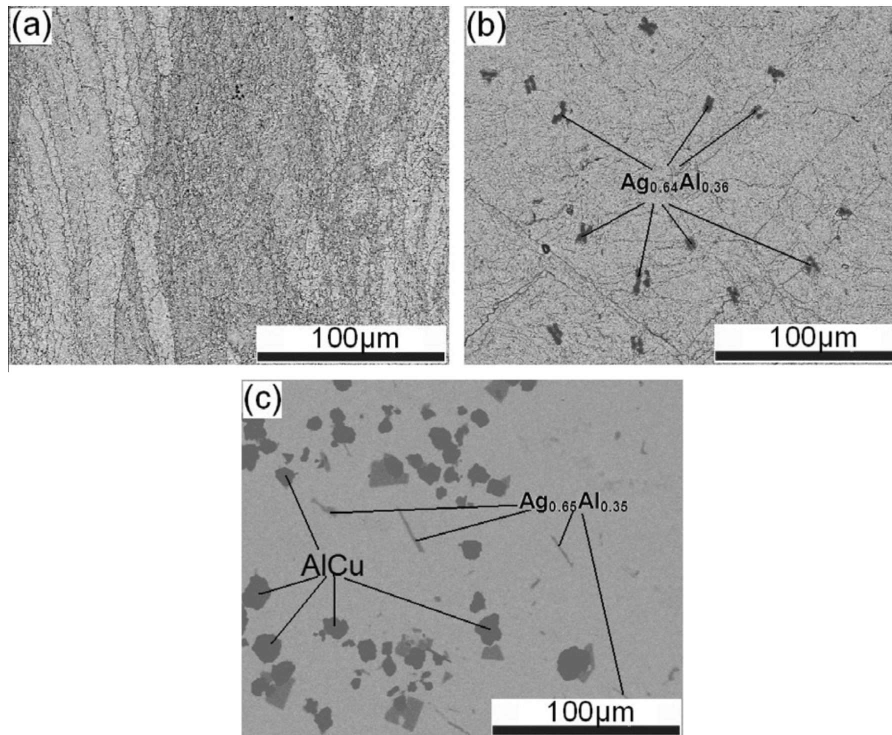

Fig. 1. SEM images taken from the polished cross sections of the three as-fabricated Al-alloyed solders: (a) Sn1Al, (b) SA1Al and (c) SAC1Al.

The effects of trace additions into Sn-based solders on the growth of IMCs at the solder/Cu interfaces are quite complicated. When trace Co, Ni and Pt nanoparticles were added into Sn–Ag solder, they were found to dissolve into the Cu–Sn IMCs and effectively reduce their growth at the solder/Cu interface [12]. When trace Co nanoparticles were added into Sn–Ag–Cu solder, Co was found to dissolve into Cu_6Sn_5 IMC, which suppressed the growth of Cu_3Sn IMC, but enhanced the growth of Cu_6Sn_5 IMC at the solder/Cu interface [22]. On the addition of 0.5–1.0 wt% Zn into Sn–Ag–Cu solder on Cu substrate, Cu_3Sn IMC was significantly suppressed and the morphology of Cu_6Sn_5 grains was changed, leading to suppressed Cu_6Sn_5 growth, while 1.5 wt% Zn added into Sn–Ag–Cu solder on Cu substrate led to the nucleation of a Cu_5Zn_8 IMC layer at the interface, followed by massive spalling of the layer into the solder, forming a barrier layer limiting Cu_6Sn_5 growth [23]. Both Mo and Al_2O_3 nanoparticles could preferably be absorbed at the boundaries of Cu_6Sn_5 IMC scallops and suppress the growth of both Cu_6Sn_5 and Cu_3Sn IMC layers at the Sn–Ag–Cu solder/Cu interface [24,25]. In addition, trace RE element Ce added into Sn–Ag–Cu solder might slightly influence the growth of IMCs between the solder and Cu substrate [26]. Alternatively, trace RE elements Ce and La could be absorbed at the interfaces between Sn and Cu_6Sn_5 IMC layer, and hence depress the activity of Sn and suppress the growth of Cu_6Sn_5 IMC in the SnBiAg-xRE/Cu samples during the reflow process [27].

In another particular previous study [28,29], it has been shown that traces of Al may be added to the eutectic 42Sn–58Bi solder to form a Cu–Al IMC layer that acts as a barrier to slow down further reactions between the solder and Cu substrate under vacuum. In the present work, 1 wt% of Al was added into the basic 100Sn, 96.5Sn–3.5Ag (SA) and 95.5Sn–3.9Ag–0.6Cu (SAC) solders to observe its effectiveness in forming a barrier layer that slows down IMC growth. The Sn, SA and SAC solders were chosen as the basic solder alloys because they have higher melting points and can be used at higher operating temperatures than the eutectic 42Sn–58Bi solder. First, the IMC growth rates between the solders with 1 wt% Al addition and a Cu substrate were examined during reflow at 260 °C under $2\%H_2 98\%N_2$ forming gas for times of 5–120 min. Then the solid state interfacial reaction in the SAC–1Al/Cu system, which exhibited the lowest IMC growth rate during the reflow process, was further investigated by isothermal ageing at 170 °C in air and the results were compared with those obtained from the SAC/Cu system.

Following the description of the experimental procedure, this paper presents results for the interfacial reaction between the molten SA and SAC solders and Cu substrate during the reflow process to provide a benchmark for IMC growth rates between the various solders with 1 wt% Al addition and the Cu substrate. Then IMC growth in the Sn–1Al/Cu, SA–1Al/Cu and SAC–1Al/Cu systems, during identical reflow conditions, are presented and analysed, with focus on the effect of 1 wt% Al addition on the IMC growth rates. This is followed by a comparison and analysis of the solid state interfacial reactions in the SAC/Cu and SAC1Al/Cu systems during isothermal ageing. Finally, the results obtained are discussed in the context of studies of the interfacial reactions between Sn-based solders and the Cu substrate.

2. Experimental procedure

2.1. Materials

The basic Sn, SA and SAC solder alloys used were commercially available 3.2 mm diameter 99.95% pure Sn wire (Alfa Aesar), 0.1 mm thick eutectic 96.5Sn–3.5Ag foil (Indium Corporation) and near eutectic 95.5Sn–3.8Ag–0.7Cu solder paste

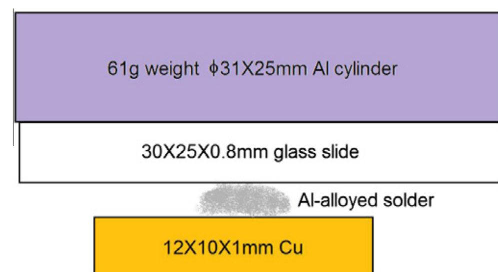

Fig. 2. Schematic illustration of pressure applied on the Al-alloyed solder/Cu samples during the reflow process.

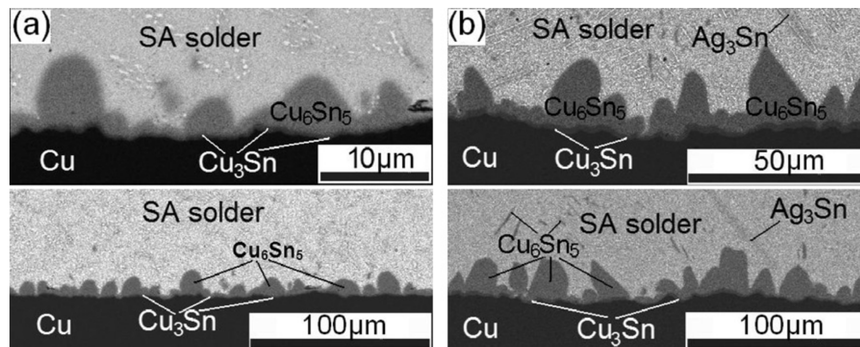

Fig. 3. SEM images taken from the polished cross sections of the SA/Cu samples reflowed at 260 °C for: (a) 5 min and (b) 120 min.

(Multicore), respectively. The flux in the as-received SAC solder paste was removed so as not to contaminate the vacuum reflow oven. This was done by reflowing the solder paste at 260 °C in air for 5 min and then cleaning it with acetone. The alloyed Sn-based solders with 1 wt% Al addition, subsequently referred to as Sn1Al, SA1Al and SAC1Al, were fabricated in-house by dissolving the corresponding amount of Al (Al–Mg alloy 5052, Alfa Aesar) into the basic solder alloys at 700 °C for 30 min. In order to prevent solder oxidization, fabrication for the three Al-alloyed solders was carried out in evacuated and sealed Pyrex glass tubes. Fig. 1 presents scanning electron microscopy (SEM) images showing the microstructures of the three as-fabricated Al-alloyed solders. It was hard to find any Al in the Sn1Al solder (Fig. 1a). Energy-dispersive X-ray spectroscopy (EDXS) microanalysis revealed that the Al addition in the SA1Al solder is in the form of ξ ($Ag_{0.64}Al_{0.36}$) IMC (Fig. 1b), while that in the SAC1Al solder in the form of both η_2 (AlCu) and ξ ($Ag_{0.65}Al_{0.35}$) IMCs (Fig. 1c). Thus, Ag and Cu existing in the basic SA and SAC solder alloys have acted as effective vehicles for the added Al to be alloyed into the solders.

The Cu substrate used was commercially available, 1 mm thick, 99.9% pure Cu foil (Alfa Aesar). It was cut into the coupons of 12 × 10 × 1 mm in size. The cut Cu coupons were first polished using 15, 3 and 1 μm diamond slurries, then cleaned using 15% HNO_3 solution under ultrasonic support, and finally rinsed using deionised water and acetone.

2.2. Preparation of samples

For all the SA, SAC, Sn1Al, SA1Al and SAC1Al solder alloys, 0.3 g of diced solder was placed on each of the cleaned Cu coupons to prepare the samples with a solder layer approximately 1 mm maximum thickness. After the solder pieces were placed on the Cu coupons, they were put into a vacuum reflow oven which was first preheated up at 200 °C and evacuated below 5 mbar for 3 min, and then held at the same temperature and purged with $2\%H_2 98\%N_2$ forming gas (450 L/min at 1.5 bar) for 5 min. The reflow was finally done at 260 °C for 5, 10, 20, 40, 60, 90 or 120 min, also under the forming gas flow of 450 L/min at 1.5 bar, before being cooled down to room temperature within 3 min. During the reflow process, a slight pressure was also applied by placing an Al cylinder on the Sn1Al, SA1Al and SAC1Al solder alloys to improve their spreading and wettability on the Cu coupons. This is illustrated schematically in Fig. 2.

As presented below, the SAC1Al/Cu system was found to have the lowest growth rate of IMCs during the reflow process. The SAC1Al/Cu samples, as well as SAC/Cu sample, that were reflowed at 260 °C for 10 min were further subjected to isothermal ageing at 170 °C in air for 24, 48, 96, 191, 384, 768 and 2096 h to investigate the solid state interfacial reactions.

Metallographic cross-sections of the reflowed samples and the samples after isothermal ageing were prepared for identification and thickness measurement of IMCs. The samples were mounted in epoxy resin that was cured at room temperature for 24 h. The mounted samples were then successively ground with 400, 800, 1000, 1200 and 2400 grit SiC papers and finally polished using diamond slurries of 3 μm and 1 μm for 10 min and 5 min, respectively.

2.3. Identification and thickness measurement of IMCs

A JEOL 6400 SEM using the backscattered electron signal was employed to observe and analyze the microstructural features and take the corresponding images from the polished cross-sectional samples. The IMCs formed between the solders and the Cu substrate were identified using an Oxford Instruments ISIS EDXS microanalysis system fitted on the SEM. Then the thicknesses of the IMC layers were measured using an image analysis method as detailed elsewhere [30,31]. The image analysis was done utilizing the Image Processing Toolbox Version 5.0.0 of MATLAB R14SP2 (The Mathworks). For each sample, three images of 512 × 416 pixels in resolution, two of 236 × 192 μm or 118 × 91 μm and one of 118 × 91 μm or 47 × 38 μm in size, were used and the obtained data series were merged together for further statistical analysis. The resulting thicknesses were given in terms of mean and 95% confidence interval.

3. Results

3.1. Interfacial reactions during reflow process

3.1.1. SA/Cu and SAC/Cu systems

SEM images and EDXS analysis revealed that the interfacial microstructure was similar in the SA/Cu and SAC/Cu samples. Two distinct layers of IMCs at the solder/Cu interfaces were observed in all the SA/Cu and SAC/Cu samples reflowed for times of 5–120 min. Fig. 3 presents the SEM images taken from the polished cross sections of two SA/Cu samples. As shown in Fig. 3, a thicker layer of η-phase (Cu_6Sn_5) compound consisting of scalloped grains was formed at the solder side, and a thinner layer of ε-phase (Cu_3Sn) compound was formed at the Cu side. In addition to these layered IMCs, some relatively smaller and needle-like Cu_6Sn_5 grains were observed within the bulk of the solder (Fig. 3b). Occasionally, needle-like Ag_3Sn grains were also found within the bulk of solder (Fig. 3b).

The results of the thicknesses of the Cu_6Sn_5 and Cu_3Sn layers in the reflowed SA/Cu and SAC/Cu samples measured using the image analysis method are presented in Figs. 4 and 5, as a function of square root of reflow time. Here and also in what follows, the dispersive IMC grains within the bulk of the solders are not included in the calculation of the thicknesses. The mean thicknesses of the Cu_6Sn_5 and Cu_3Sn layers in both the SA/Cu and SAC/Cu systems increase with increase in reflow time.

Comparing the thicknesses of IMCs in the two systems, the mean thickness of the Cu_6Sn_5 layer in a SAC/Cu sample is 1.2 to 1.9 μm thicker than that in the corresponding SA/Cu sample. The experimental points of the Cu_6Sn_5 IMC layer in the SA/Cu system fluctuate around a linear pattern more than those of the Cu_6Sn_5 IMC layer in the SAC/Cu system. By contrast, the thickness of the Cu_3Sn layer is slightly thicker than, or similar to, that in the corresponding SA/Cu sample reflowed under an identical condition.

3.1.2. Sn1Al/Cu system

With 1 wt% Al added into pure Sn, no change occurred in the formation of IMCs at the solder/Cu interfaces when compared to the SA/Cu and SAC/Cu systems, with the exception of the Sn1Al/Cu sample reflowed at 260 °C for 120 min (Fig. 6). However, the growth rates of both Cu_6Sn_5 and Cu_3Sn layers had somewhat been reduced. In the Sn1Al/Cu sample reflowed at 260 °C for 40 min, a thin layer of Al–Cu IMC, identified as γ ($Al_{0.33}Cu_{0.67}$) IMC using EDXS, was found to form within the bulk of the solder (Fig. 6b). In the Sn1Al/Cu sample reflowed at 260 °C for 120 min, part of the interface consisted of two adjacent Cu_6Sn_5 and Cu_3Sn layers,

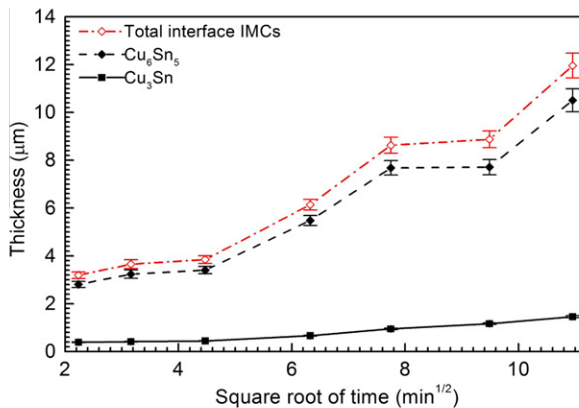

Fig. 4. Plots of thickness versus square root of time for IMCs formed at interfaces in the SA/Cu samples during the reflow process at 260 °C.

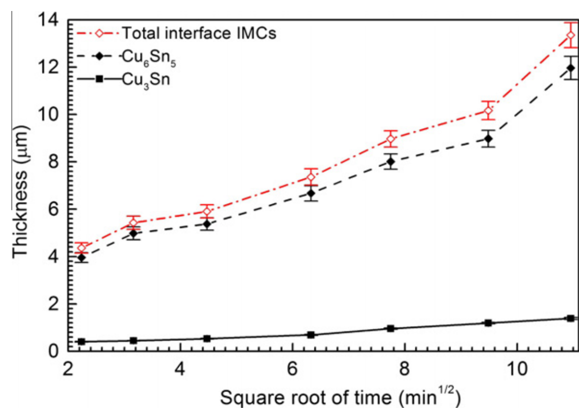

Fig. 5. Plots of thickness versus square root of time for IMCs formed at interfaces in the SAC/Cu samples during the reflow process at 260 °C.

while other part of the interface was a thinner layer of γ ($Al_{0.33}Cu_{0.67}$) IMC (Fig. 6d). It was especially noted that the consumption rate of the substrate Cu at the former part of the interface was significantly higher, about 50 μm more being consumed, than that at the latter part of the interface. Many γ ($Al_{0.33}Cu_{0.67}$) grains were also observed around the top part of the solder (Fig. 6d).

Results of the thicknesses of the layered Cu_6Sn_5, Cu_3Sn and γ Al–Cu IMCs measured in the reflowed Sn1Al/Cu samples are presented in Fig. 7. Here and also in what follows, the measured thicknesses for the layered Al–Cu IMC within the bulk of the solder are given as those of the Al–Cu IMC within solder matrix. In the case of two different types of interfacial microstructure, e.g. where part of the interface consisted of two adjacent Cu_6Sn_5 and Cu_3Sn layers, while the other part of the interface consisted of a thinner layer of Al–Cu IMC, were observed in one sample, two points of total interface IMCs are accordingly given. As a whole, the mean thicknesses of both Cu_6Sn_5 and Cu_3Sn layers fluctuate with respect to reflow time. Nevertheless, the total thickness of the IMCs at the solder/Cu interface in one Sn1Al/Cu sample is clearly smaller than that in the corresponding SA/Cu and SAC/Cu samples reflowed for an identical time.

3.1.3. SA1Al/Cu system

With 1 wt% Al added into the eutectic Sn–Ag solder, Cu_6Sn_5 and Cu_3Sn were also the IMCs formed at the interfaces (Fig. 8). However, Al–Cu-containing IMCs were observed in more SA1Al/Cu samples than the Sn1Al/Cu samples. They included the samples reflowed at 260 °C for 5, 10, 20 and 40 min. Dispersive Al–Cu-containing grains tending to form layered IMC were found in the bulk of the solder in the sample reflowed for 5 min (Fig. 8a). A layer of Al–Cu-containing IMC existed in the bulk of the solder in the samples reflowed for 10, 20, and 40 min, and existed as the only IMC at the interface in another sample reflowed for 20 min. Certain amounts of Sn were detected using EDXS in this Al–Cu-containing IMC. This may be due to the effect of EDXS beam spreading, and may not reflect the composition of the IMC layer alone. The Cu–Sn-containing IMCs could be either Al–Cu–Sn IMCs or Al–Cu IMCs.

Results of the thicknesses of the layered IMCs in the reflowed SA1Al/Cu samples are shown in Fig. 9. The mean thicknesses of Cu_6Sn_5, Cu_3Sn and Al- Cu-containing IMCs, as well as the total thicknesses of the IMCs at the solder/Cu interface, in these reflowed SA1Al/Cu samples are more or less similar to those for the reflowed Sn1Al/Cu samples. Also similarly, the mean thicknesses of both Cu_6Sn_5 and Cu_3Sn layers fluctuate with respect to reflow time.

3.1.4. SAC1Al/Cu system

In most reflowed SAC1Al/Cu samples, two adjacent Cu_6Sn_5 and Cu_3Sn layers were the IMCs which formed at the interfaces (Fig. 10). With the exception of the sample reflowed at 260 °C for 40 min, layered Al–Cu IMCs were formed in all the other reflowed SAC1Al/Cu samples. In the sample reflowed for 5 min, part of the interface consisted of two adjacent Cu_6Sn_5 and Cu_3Sn layers, and layered Al–Cu IMC, identified as η_2 (AlCu) phase using EDXS, was found in the bulk of the solder (Fig. 10a). The other part of the interface consisted of η_2 (AlCu) IMC plus extremely thin residual Cu_3Sn at the Cu substrate side, where approximately 30 μm less Cu had been consumed than at the former part of the interface (Fig. 10a). In one sample reflowed for 10 min, the interface consisted of adjacent Cu_6Sn_5 and Cu_3Sn layers, and layered AlCu IMC was formed within the bulk of the solder. In another sample reflowed for 10 min, only η_2 (AlCu) layer was observed at the interface (Fig. 10b). In the SAC1Al/Cu samples reflowed for times longer than 10 min, layered Al–Cu IMCs, if present, were all identified as δ (Al_2Cu_3) phase using EDXS.

Results of the thicknesses of the layered IMCs in the reflowed SAC1Al/Cu samples are shown in Fig. 11. Similar to those in Fig. 9, the mean thicknesses of the layered IMCs fluctuate with respect to reflow time. On the whole, the thicknesses of Cu_6Sn_5 and Cu_3Sn and the total thicknesses of IMCs at the interfaces are further reduced when compared to those in the corresponding Sn1Al/Cu and SA1Al/Cu samples.

3.2. Interfacial reactions during isothermal ageing

3.2.1. SAC/Cu system

With increase in ageing time at 170 °C, the interface between the Cu_6Sn_5 layer and SAC solder in the SAC/Cu samples gradually became planar compared to the as-reflowed SAC/Cu sample (Fig. 12). However, a few protruding Cu_6Sn_5 grains were still on the Cu_6Sn_5 layer in the SAC/Cu sample even after an ageing time of 2076 h (Fig. 12b).

The results of the thicknesses of the Cu_6Sn_5 and Cu_3Sn layers in the aged SAC/Cu samples are presented Fig. 13. For aging times between 24 and 191 h, the mean thickness of the Cu_6Sn_5 layer appears to be thinner than that of the as-flowed sample. For ageing times of 384–2096 h, the mean thickness of the Cu_6Sn_5 layer increases with increasing ageing time. By contrast, the mean thickness of Cu_3Sn layers increases with ageing time from the start. Comparing the mean thicknesses of the Cu_6Sn_5 and Cu_3Sn layers, the ratio of the former to the latter decreases with increasing the ageing time, and the former becomes thinner than the latter at an ageing time of between 384 and 768 h.

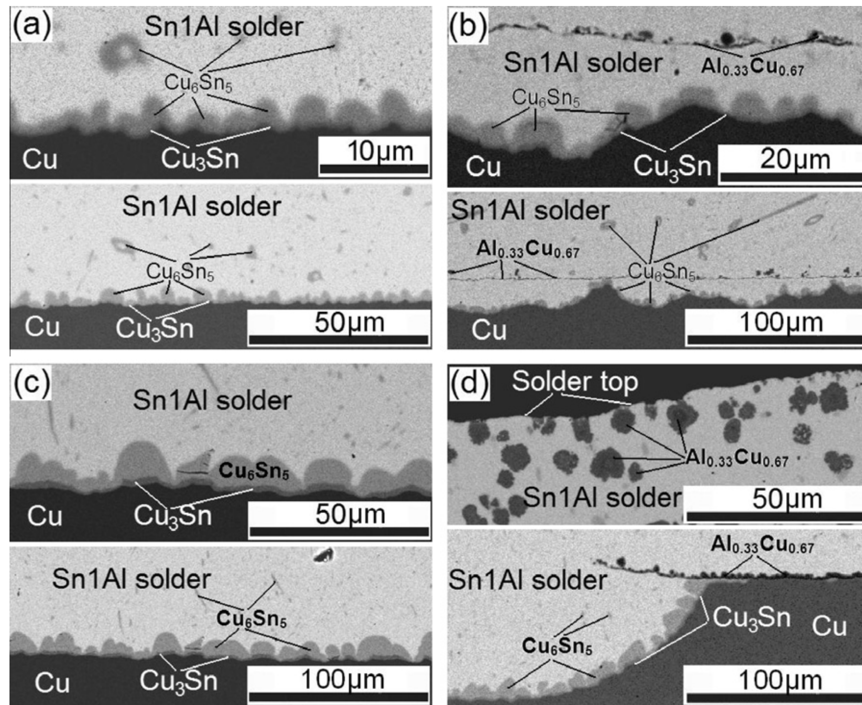

Fig. 6. SEM images taken from the polished cross sections of the Sn1Al/Cu samples reflowed at 260 °C for: (a) 10 min, (b) 40 min, (c) 90 min and (d) 120 min.

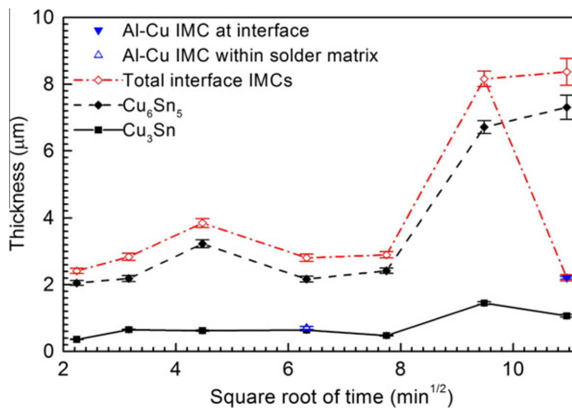

Fig. 7. Plots of thickness versus square root of time for IMCs formed at interfaces in the Sn1Al/Cu samples during the reflow process at 260 °C.

3.2.2. SAC1Al/Cu system

In the SAC1Al/Cu sample aged for 24 h, a layered η_2 (AlCu) IMC was still within the bulk of the SAC1Al solder (Fig. 14a). With the exception of the sample aged for 384 h, a layer of η_2 (AlCu) IMC was observed at part or across the entire interface in the samples aged for the times between 48 and 768 h (Fig. 14b). In the sample aged for 384 h, a layer of η_2 (AlCu) IMC, 1.39 μm in mean thickness, was found within the bulk of the solder. On the other hand, in the sample aged for 2096 h, the layered Al–Cu IMC was found to move back into the bulk of the solder and gradually be transformed into dispersive δ (Al_2Cu_3) IMC grains. Consequently, two adjacent layers of Cu_6Sn_5 and Cu_3Sn IMCs were formed again at the interface (Fig. 14 c).

Results of the thicknesses of the layered IMCs in the aged SAC1Al/Cu samples are presented in Fig. 15. Similar to the results for the reflowed SAC1Al/Cu samples in Fig. 11, the mean thicknesses of these IMC layers fluctuate significantly with respect to ageing time. On the whole, the thicknesses of Cu_6Sn_5 and Cu_3Sn and the total thicknesses of IMCs at the interfaces are significantly lower than those in the corresponding SAC/Cu samples (Fig. 13).

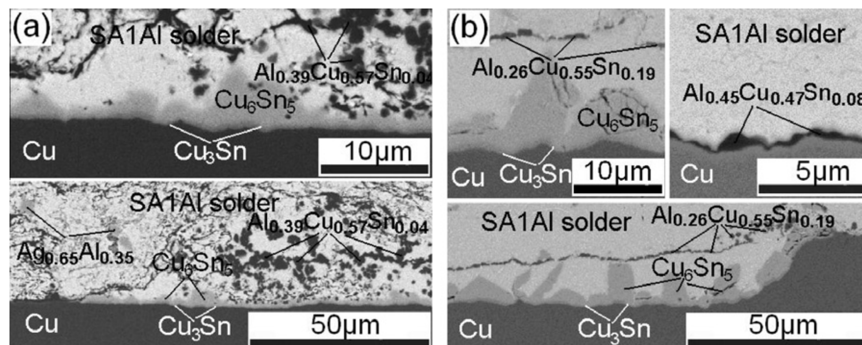

Fig. 8. SEM images taken from the polished cross sections of the SA1Al/Cu samples reflowed at 260 °C for: (a) 5 min and (b) 120 min.

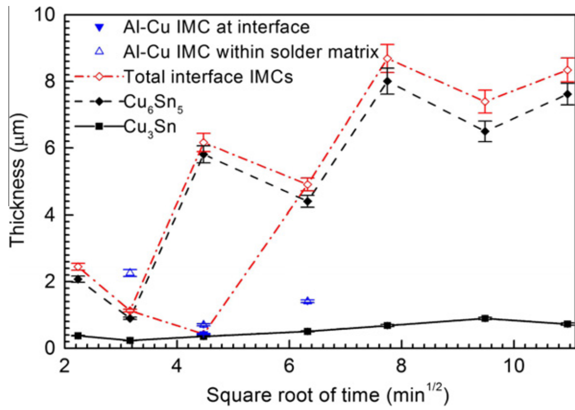

Fig. 9. Plots of thickness versus square root of time for IMCs formed at interfaces in the SA1Al/Cu samples during the reflow process at 260 °C.

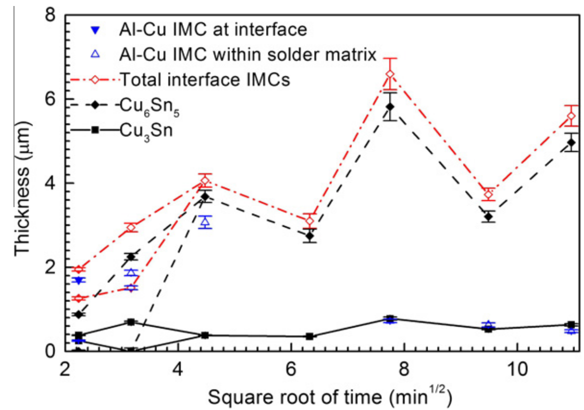

Fig. 11. Plots of thickness versus square root of time for IMCs formed at interfaces in the SAC1Al/Cu samples during the reflow process at 260 °C.

4. Discussion

4.1. Interfacial reactions during reflow process

4.1.1. Growth of Cu_6Sn_5 and Cu_3Sn in SA/Cu and SAC/Cu systems

The interfacial structures formed between molten Sn–3.5Ag, Sn–3.8Ag–0.7Cu solders and Cu substrates have previously been reported by a number of authors [18,20,21,32]. The present interfacial structure of two layers of IMCs Cu_6Sn_5 and Cu_3Sn is the same as that reported by Takaku et al. [21] for the interfacial reaction between molten Sn–3.5Ag solder and Cu substrate at 250 °C for times ranging from 1 min to 5 h. It is also the same as those reported by Liang et al. [32] for the interfacial reaction between molten Sn–3.5Ag and Sn–3.8Ag–0.7Cu solders and a Cu substrate at 225–280 °C for times longer than 3 min down to times longer than 30 s, respectively. In other studies of the IMCs formed between molten Sn–3.5Ag and Sn–3.5Ag–0.7Cu solders and Cu substrates at 250 °C for times of 10–90 s, only a single layer of Cu_6Sn_5 was observed [18,20]. These studies showed that a high superheat, i.e. a temperature above the liquidus temperature of the solder and/or a longer time, would favor the formation of two adjacent Cu_6Sn_5 and Cu_3Sn layers at the molten solder/substrate interface. The formation of an interfacial structure of two layers of IMCs, Cu_6Sn_5 and Cu_3Sn, observed in the present SA/Cu and SAC/Cu systems can be explained because the growth of Cu_3Sn during all experimental temporal scales appears to be diffusion-controlled [2,5,6,18]. The formation of Cu_3Sn occurs because diffusion-controlled growth implies that all IMCs of the phase diagram should appear in the corresponding proportions according to time and local composition.

The thicknesses of the Cu_6Sn_5 and Cu_3Sn presented in Figs. 4 and 5 are in good agreement with those of Cu_6Sn_5 and Cu_3Sn formed between the molten Sn–3.5Ag and Sn–3.8Ag–0.7Cu solders and a Cu substrate at 260 °C for similar reflow times, as reported in Ref. [32]. During the early reflow stage, the formation and growth of Cu_6Sn_5 and Cu_3Sn IMCs is quite complicated and may involve multiple simultaneous processes [11–14]. These may include the

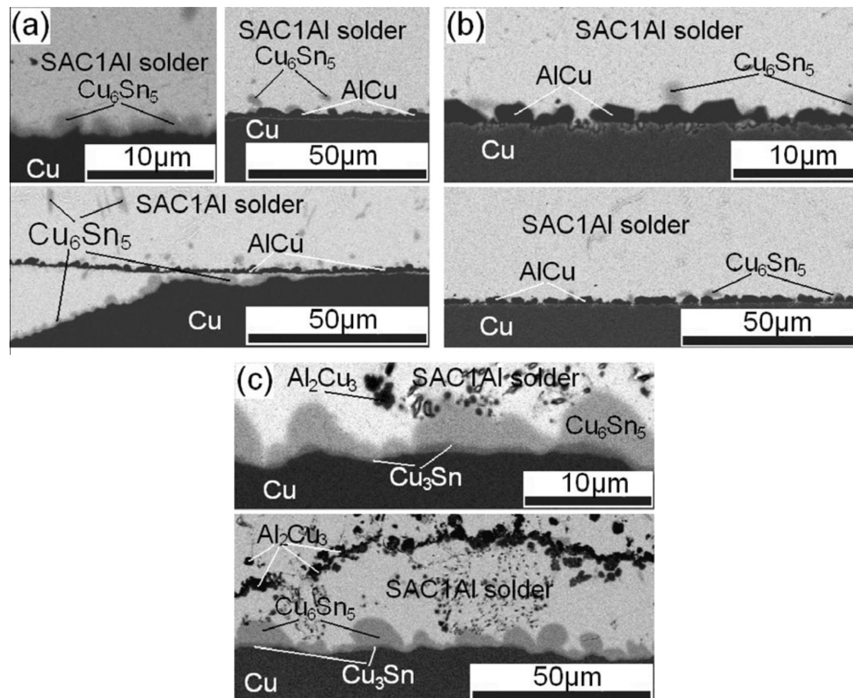

Fig. 10. SEM images taken from the polished cross sections of the SAC1Al/Cu samples reflowed at 260 °C for: (a) 5 min, (b) 10 min and (c) 20 min.

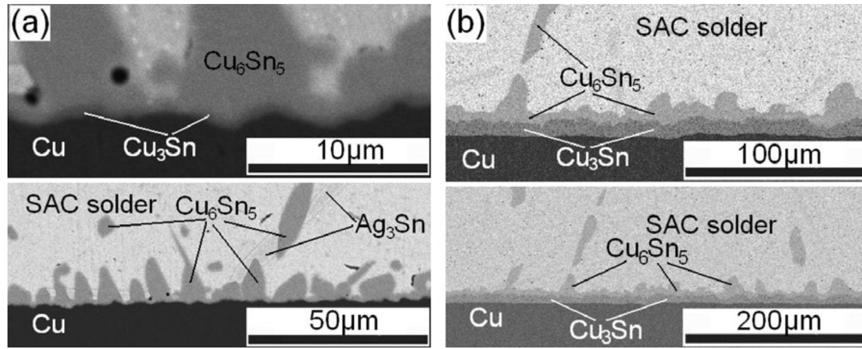

Fig. 12. SEM images taken from the polished cross sections of the SAC/Cu samples aged at 170 °C for: (a) 0 h and (b) 2076 h.

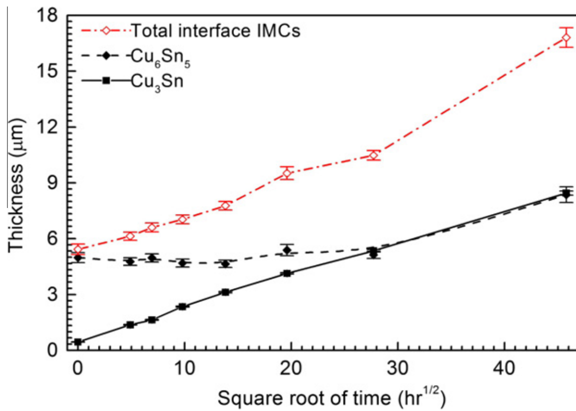

Fig. 13. Plots of thickness versus square root of time for IMCs formed at interfaces in the SAC/Cu samples during thermal ageing at 170 °C.

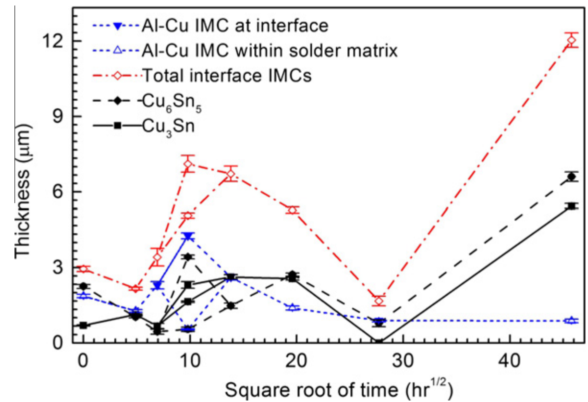

Fig. 15. Plots of thickness versus square root of time for IMCs formed at interfaces in the SAC1Al/Cu samples during thermal ageing at 170 °C.

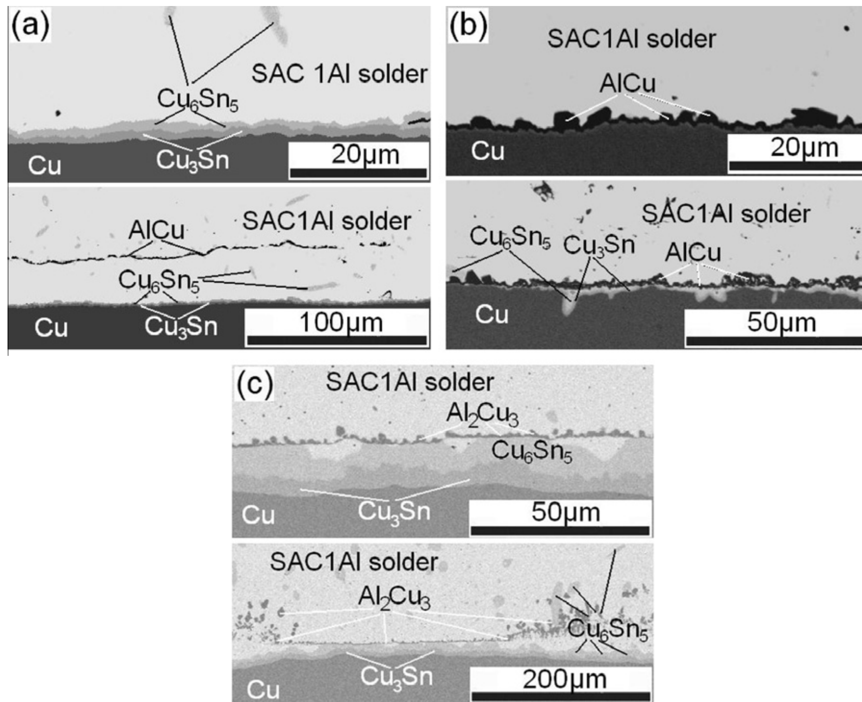

Fig. 14. SEM images taken from the polished cross sections of the SAC1Al/Cu samples aged at 170 °C for: (a) 24 h, (b) 48 h and (c) 2076 h.

dissolution of Cu atoms from the Cu substrate and/or the formed Cu_6Sn_5 IMC into the liquid Sn-based solder, the reaction between Cu atoms and Sn atoms, the precipitation/nucleation of Cu–Sn IMCs on the top of Cu substrate, the solidification of Cu–Sn IMCs from supersaturated liquid solder, and lattice and/or grain boundary diffusion of Cu and Sn atoms in the formed Cu–Sn IMCs.

Comparing the SA/Cu and SAC/Cu systems, the SAC solder was saturated by Cu atoms earlier than the SA solder. The reduction in thickness of Cu_6Sn_5 due to dissolution into the SAC solder was lower in the SAC/Cu sample than in the SA/Cu sample during the early reflow stage. On the other hand, the concentration of Cu in the molten SAC solder might be closer to the saturation concentration due to the existence of 0.7% Cu, or the saturation concentration of Cu in the molten SAC solder is a little higher than for the SA solder due to the additional 0.3% Ag [33]. Either of these would lead to more supersaturated Cu atoms contributing to the epitaxial growth of previously formed Cu_6Sn_5 scallops at the interface during the solidification of the molten SAC solder. As a result, the mean thickness of the Cu_6Sn_5 layer in the SAC/Cu sample is 1.2 to 1.9 μm thicker, while the thickness of the Cu_3Sn layer is slightly thicker than or similar to that in the corresponding SA/Cu sample reflowed under an identical condition.

In addition, grain boundary grooving, grain coarsening, grain faceting and grain coalescing influence the growth kinetics of the IMCs [15]. It is also arguable that solidification of the IMC from the supersaturated liquid solder may still contribute the growth of the Cu_6Sn_5 and Cu_3Sn IMCs during the prolonged reflow stage to some extent. The precipitation out of the Cu atoms supersaturated in the liquid solder took place when the samples were cooled down from the reflow temperature, part of which might cause epitaxial growth of the previously formed Cu_6Sn_5 scallops at the interfaces. Because these complicated mechanisms might have been involved in the growth kinetics and the resulting thicknesses are just used as benchmarks in the present work, no attempt will be made to model the growth kinetics of Cu_6Sn_5 and Cu_3Sn IMCs in the SA/Cu and SAC/Cu systems.

4.1.2. Effect of Al addition on IMC growth

With the addition of 1 wt% Al into pure Sn solder, Al-containing IMC, γ ($Al_{0.33}Cu_{0.67}$), was found in only two of the seven reflowed Sn1Al/Cu samples. This may be due to the fact that the addition of 1 wt% Al was not distributed uniformly within the as-prepared Sn1Al solder. Further evidence can be provided by the EDXS result which failed to defect Al in three polished 5×3 mm Sn1Al solder samples that were randomly cut from an as-prepared Sn1Al solder clump approximately of ϕ 15×10 mm in size.

The growth rates of IMCs in all the reflowed Sn1Al/Cu samples were lower than the corresponding SA/Cu samples (Figs. 4 and 7). This may be due to the fact that the saturation concentration of Cu in the molten Sn1Al solder may be higher than in the SA solder. Consequently, the Cu_6Sn_5 IMC formed during the early stages of the reflow process was dissolved into the Sn1Al solder more than into the SA solder. This led to a corresponding reduction in the thicknesses of Cu_6Sn_5 in the reflowed Sn1Al/Cu samples. Another possibility was the reduction in activity of Sn due to the existence of trace Al within the molten solder though not detected using EDXS. On the other hand, a clearly lower consumption rate of Cu substrate under the γ ($Al_{0.33}Cu_{0.67}$) IMC compared to the other parts of the interface reveals that this layer of Al-containing IMC can act as an effective barrier to slow down the interfacial reaction (Fig. 6d).

With the addition of 1 wt% Al into the basic SA solder, Al-containing IMCs, Al–Cu–Sn or Al–Cu IMCs, were found in more SA1Al/Cu samples than γ ($Al_{0.33}Cu_{0.67}$) IMC found in the Sn1Al/Cu samples (Figs. 7 and 9). This indicates that the Ag in the basic SA solder, acting as a vehicle to carry the Al, had improved the uniformity of Al within the SA1Al solder to some extent. In the reflowed SA1Al/Cu samples, the reduced growth rates of IMCs compared with those in the reflowed SA/Cu samples can be ascribed to either of the following two reasons. If the Al-containing IMC never reached the interface between the molten solder and Cu substrate in a SA–1Al/Cu sample, one possibility is a reduction in activity of Sn due to the existence of trace Al within the molten solder. Another possibility is reduction in reaction time for the relatively rapid growth of two adjacent Cu_6Sn_5 and Cu_3Sn layers at the interface of a SA1Al/Cu sample. In this case, the layered Al-containing IMC migrated towards and replaced the Cu_6Sn_5 and Cu_3Sn layers, and then stayed at the interface for some time.

Of the SAC1Al/Cu samples, only in the one reflowed for 40 min was no layered Al-containing IMC found. Thus, the Cu and Ag in the basic SAC solder, acting as vehicles for the Al, had further improved the uniformity of Al within the as-fabricated SAC1Al solder. Comparing the compositions and locations of the Al-containing IMCs in the different samples, they clearly evolved with reflow time as follows: a layered η_2 (AlCu) IMC was first formed within the bulk of the molten SAC1Al solder; then it gradually migrated towards and reached the interface with the Cu_6Sn_5 and Cu_3Sn layers at a reflow time of between 5 and 10 min; after this, it gradually replaced the Cu_6Sn_5 and Cu_3Sn layers at the interface for a time of 10 to 20 min; after finishing the replacement, it was transformed into δ (Al_2Cu_3) phase through a further reaction with Cu and finally moved back into the bulk of the solder after a time of approximately 20 min. Therefore, the significant reduction in growth rates of IMCs in the reflowed SAC1Al/Cu samples compared with those in the reflowed SA/Cu and SAC/Cu samples can be attributed to the above evolution of the Al-containing IMCs during the reflow process. This reduced the reaction time for the formation and growth of the two adjacent Cu_6Sn_5 and Cu_3Sn layers. Nonetheless, the thickness of the Cu_6Sn_5 layer formed prior to the η_2 (AlCu) IMC reaching the interface was significantly thinner than that in the corresponding SAC/Cu and SA/Cu samples (Figs. 3a, 8a and 10a). This reveals that a reduction in activity of Sn due to the existence of trace Al in the molten solder was also an important mechanism to reduce the growth rates of IMCs in the SAC1Al/Cu samples.

In the work of Nowottnick et al. [28,29], which was conducted under vacuum conditions, traces of Al added into Sn–58Bi solder promoted the formation of a stable Cu–Al IMC barrier layer at the molten solder/Cu interface at 200° for 500 h. This is different from the above evolution of Al-containing IMCs in the present work. This difference may be caused by the different solder alloy, or different reflow condition, or perhaps both of these.

In addition, even for the SAC1Al solder which was the best of the three Al-alloyed solders investigated, the uniformity of Al within the solder still needs to be further improved. This might be done through re-manufacturing the as-fabricated SAC1Al solder clumps into powder particles and then incorporating them into solder pastes.

4.2. Interfacial reactions during isothermal ageing

4.2.1. IMC growth in SAC/Cu system

For the solid state interfacial reaction in the SAC/Cu samples during isothermal ageing, the growth of two adjacent Cu_6Sn_5 and Cu_3Sn layers should mainly be controlled by the diffusion of Cu and Sn atoms through the previously formed Cu_6Sn_5 and Cu_3Sn layers. However, a new growth equilibrium between Cu_6Sn_5 and Cu_3Sn layers had to be established during the early ageing stage because the SAC/Cu samples had first been reflowed at higher temperature prior to isothermal ageing. This is why for aging times between 24 and 191 h, the mean thickness of the Cu_6Sn_5 layer is thinner than that of the as reflowed sample.

Additional growth of the Cu_6Sn_5 layer was also caused by the isolated Cu_6Sn_5 grains which were within the bulk of the solder but close to the Cu_6Sn_5 layer. As aforementioned, these isolated Cu_6Sn_5 grains were formed in the as-reflowed SAC/Cu samples because of precipitation out of supersaturated Cu atoms in the molten solder during the cooling stage of the reflow process. During the isothermal ageing process, they might form a mass flow due

to coalescence to cause an additional growth superimposing on the diffusion-controlled growth of the Cu_6Sn_5 layer. With increasing ageing time, the number of isolated Cu_6Sn_5 grains was decreased and/or they were further from the Cu_6Sn_5 layer at the interface. As a result, their contribution to the growth of the Cu_6Sn_5 layer was reduced. This explanation can be further supported by the protruding Cu_6Sn_5 grains on the relatively planar Cu_6Sn_5 layer.

Nevertheless, the measured thicknesses of the Cu_6Sn_5 and Cu_3Sn layers in the SAC/Cu samples during the isothermal ageing can be described reasonably well with a numerical model developed for the diffusion-controlled growth of two adjacent Cu_6Sn_5 and Cu_3Sn layers. The relevant detail is outside the scope of this paper, and will be reported elsewhere [34]. The extracted interdiffusion coefficients, $D_{int,Cu3Sn}$ and $D_{int,Cu6Sn5}$, are respectively 8.25×10^{-19} m^2/s and 9.97×10^{-19} m^2/s. They are both lower than all those interpolated or extrapolated and calculated from the results of the Cu/Sn, Cu/Cu_6Sn_5 and Cu_3Sn/Sn diffusion couples as reviewed in Ref. [6]. This may be associated with the present reflow process under forming gas used to prepare the as-reflowed samples. In a previous work [18], it was reported that the activation energy of reaction rate constant for the growth of Cu_6Sn_5 IMC in Sn–3.5Ag/Cu samples during isothermal ageing depended on method of sample preparation. The activation energy for the samples prepared using the dipping method was found to be lower than that for the samples prepared using the reflow method.

4.2.2. Effect of Al addition on IMC growth

The evolution of Al-containing IMC in the SAC1Al/Cu samples aged in air was similar to that in the SAC1Al/Cu samples reflowed under forming gas. With increasing ageing time, the layered η_2 (AlCu) IMC previously in the bulk of the solder migrated towards and replaced the Cu_6Sn_5 and Cu_3Sn layers at the interface between the solder and the Cu substrate. After staying at the interface for some time, e.g., longer than one month, it was finally transformed into δ (Al_2Cu_3) IMC and moved back into the bulk of the solder at an ageing time approximately of three months. The exception of the SAC1Al/Cu sample aged for 384 h where the layered η_2 (AlCu) IMC was found within the bulk of the solder can be ascribed to the fact that the distribution of the added Al was not uniform among the solder pieces.

It is generally accepted that for any addition into the Sn-based solders to influence Cu–Sn IMC growth in solid interfacial reactions, it should either be soluble in the IMCs to change their stability or in the solid Sn to change its activity [12,22,23]. Otherwise there is no energetic way that the addition could have effect on the driving forces for Sn and Cu diffusion through the Cu–Sn IMCs. The present experimental results show that there is hardly any Al detectable inside either of the Cu_6Sn_5 and Cu_3Sn IMCs, rather there is formation of additional η_2 (AlCu) or δ (Al_2Cu_3) IMC layers at the interface or within the bulk of the solder. The layered η_2 (AlCu) IMC at the interface of an aged SAC1Al/Cu sample can act as an effective barrier and thus reduce the total thickness of IMCs significantly. The total thickness of IMCs in the aged SAC1Al/Cu sample was also clearly thinner than that in the corresponding SAC/Cu sample. In this case, the existence of Al in the solder, albeit with low solubility, might reduce the activity of Sn involved in the interfacial reaction. Therefore, addition of trace Al into the SAC solder is a valid technique to slow down the growth rates of IMCs between the solder and Cu substrate even when subjected to isothermal ageing in air.

During the early stage, the η_2 (AlCu) IMC layer within the bulk of the solder was relatively Al-rich. Therefore, it was probably driven towards the interface to react with Cu and replaced the Cu_6Sn_5 and Cu_3Sn layers at the interface between the solder and the Cu substrate. Because of the limited supply of Al and more Cu diffusion through the previously formed η_2 (AlCu) IMC, the η_2 (AlCu) IMC at the interface was finally transformed into the δ (Al_2Cu_3) IMC with increasing reaction time. The δ (Al_2Cu_3) IMC layer is less stable than η_2 (AlCu) IMC at the interface, and thus gradually moved back into the bulk of the solder.

In a recent study [35], 0.5 wt% to 2 wt% Al was added into Sn–3.5Ag solder, and the solder/Cu and solder/NiP samples were prepared by soldering in air at 260 °C for 60 s and storage in air at 150 °C for up to 1000 h. It was found that with increasing the concentration of Al in the solder, the concentration of Al–Cu and Al–Ni IMC particles in the solder matrix increases, without affecting the growth rates of Cu–Sn and Ni–Sn IMC layers at the solder/substrate interfaces. This is different from the present results as mentioned above, and is again probably related to the process used to prepare the present SAC1Al/Cu samples which were reflowed under $2\%H_2 98\%N_2$ forming gas.

5. Conclusions

The effect of 1 wt% Al addition, into the basic 100Sn, 96.5Sn–3.5Ag (SA) and 95.5Sn–3.8Ag–0.7Cu (SAC) solders, on the growth rates of intermetallic compound (IMC) layers between the solders and a Cu substrate has been investigated. The following conclusions are drawn:

(1) The growth rates and thicknesses of Cu_6Sn_5 and Cu_3Sn layers in the SA/Cu and SAC/Cu systems are comparable with those for similar reflow times reported in the existing literature.
(2) Addition of 1 wt% Al into the basic 100Sn, SA and SAC solders slows down the growth rates of IMCs formed at solder/Cu interfaces. The best result has been achieved in the SAC solder with addition of 1 wt% Al. The reduction in the growth rates of IMCs can be attributed to the formation and evolution of a layer of Al-containing IMCs within the bulk of the solders and at the interfaces, as well as reduction in the activity of Sn due to the existence of trace Al in the solders.
(3) The growth rates of Cu_6Sn_5 and Cu_3Sn layers in the SAC/Cu samples during isothermal ageing are both lower than all those interpolated or extrapolated and calculated from the results of the Cu/Sn, Cu/Cu_6Sn_5 and Cu_3Sn/Sn diffusion couples reported in the existing literature. This may be associated with the present reflow process under forming gas used to prepare the as-reflowed samples with different grain size, orientation and boundary percentage.
(4) The addition of 1 wt% Al into the basic SAC solder can also significantly slow down the growth rates of IMCs in samples subjected to isothermal ageing in air. This is accompanied with an evolution of layered Al-containing IMCs within the bulk of the solder, similar to that found during the reflow process under forming gas.

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