Reliability of electronics assembled using SAC + Zn solder pastes

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Abstract

A method of preparing SAC solder with addition of 1.0-1.5wt.% Zn to Sn-3.8Ag-0.7Cu solder alloy such that a standard solder paste reflow process results in good soldering is described. Solder-substrate couples were aged at 150°C for 1000h, and results on temperature cycling (-20 to 175°C) and shear testing of solder joints is also described. The added Zn segregated to the interfacial IMCs so that Cu_6Sn_5 became $(Cu,Zn)_6Sn_5$ and $(Cu,Ni)_6Sn_5$ became $(Cu,Ni,Zn)_6Sn_5$. The reliability of assemblies utilizing Electroless Nickel Immersion Gold (ENIG) using the Zn enhanced solder is compared to that of standard SAC solder alloy for potentially reliable operation at temperature up to 185°C.

Keywords: Soldering; Lead-free solder; Intermetallic growth suppression; Sn-Ag-Cu alloys

1. Introduction

The increasing automation and control of automobile and aerospace vehicle engines, with the help of inbuilt electronic devices, together with the requirements from oil and gas drilling into deeper and hence hotter wells, have been the driving force behind the development of robust electronic joining technologies. During service in these environments, electronic components experience higher temperatures and harsh service conditions such as mechanical shock, continuous vibration and thermal cycling, leading to failure of solder joints. To date, solders for high temperature electronics have been mainly based on high Pb content alloys. Recently, European Union and other parts of the world have banned the use of Pb in solders because of its toxicity [1-3] and while some exemptions remain for cases where no practical alternatives to high Pb solders exist, these are under periodic review. The main alternative to high Pb solder are solders containing a high percentage of precious metal (e.g. Au20Sn) which are not suitable for many applications on economic grounds.

To replace the Pb-containing solder alloys for conventional applications, new Sn-based lead-free solder alloys have been developed, introducing a whole new set of materials challenges [4]. As a result Sn–Cu, Sn–Ag, and Sn–Ag–Cu (SAC) have emerged as some of the most popular replacements for Sn–Pb solders [2]. As the melting point of these solders are typically 40 °C higher than eutectic Sn-Pb, there is a potential for good performance at temperatures up to a maximum of ~200 °C but several issues remain such as void formation in interfacial IMCs, high IMC growth rates, and spalling of the initial interfacial IMCs during high temperature storage [5]. The reliability of the solder depends on the thickness of the interfacial IMC and the bulk solder microstructure.

The current work therefore focuses on the suppression of interfacial IMC on Electroless Ni Immersion Gold (ENIG) bond pads on polyimide boards and on Cu substrates. We have chosen a SAC solder (SAC 387) and modified it by addition of various amount (1.0-1.5 wt.%) of Zn. This paper discusses high temperature storage carried out at 150 °C and at 185 °C for 1000h, shear tests on solder joints after ageing and thermal cycling from -20 to 175°C for 300 cycles (these last tests are ongoing).

2. Experiment

For the experiments involving solder paste, SAC solder alloys (Sn-3.8Ag-0.7Cu) were supplied by Henkel Ltd. (Sn-3.5Ag-0.7Cu particles of 20-38 micron diameter) and mixed with Zn powder and Henkel LF318 flux (12-14 volume% of total solder paste). The Zn powder was supplied by Goodfellow, UK and the compositions were 86% metal in the paste and SAC-(0-1.5)Zn nominal alloy composition assuming all the added Zn is incorporated into the solder rather than expelled with the flux during reflow. Some experiments were also carried out on SAC solder alloyed directly with Zn forming ingots. These were fabricated in-house by dissolving the corresponding metallic foils at 420 °C for 20 min in a ceramic crucible using an electrical resistance furnace. Predetermined weights of solder were cut from the ingot and cleaned using acetone before soldering.

For the solder ingots, two type of substrate were used for ageing at 185 °C: (i) Ni-P substrates supplied by Schlumberger (Clamart, France), and consisting of Electroless Ni Immersion Gold

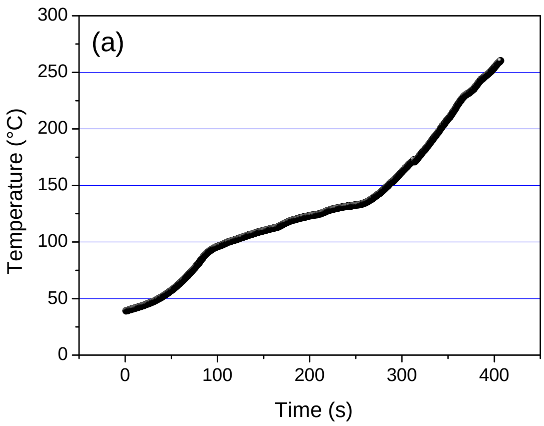
(ENIG) bond pads on polyimide boards and (ii) Cu substrates consisting of Cu coated FR4. The Cu substrates were cut into 5 mm square plates with Cu thickness of 35 μm. Before reflowing, the substrates were cleaned using IPA, acetone and finally deionised water. For the solder pastes, ageing experiments at 150 °C followed by shear tests and separately, thermal cycling was carried out using a standard FR4 printed circuit board (PCB) and Ni plated resistor components.

For both the solder ingots and the solder paste, reflow was carried out in air by preheating at 140 °C for 150 s and soldering at 260 °C for 60 s. The reflow profile diagram is illustrated in Fig.1a. The molten solder was then allowed to cool to room temperature by natural convection in air. Thermal cycling reliability tests utilized a temperature range -20 to 175 °C, the thermal cycle duration was 200 minutes, with 30 minutes at each extreme as illustrated in Fig.1b.

initial Zn concentration in the solder paste and on the fraction of Zn particles retained in the solder after reflow. Hence 1.5 wt.% Zn results in Cu–Zn IMC formation, followed by massive spalling of this layer into the solder (Fig. 2c). However, some Zn particles were expelled along with the flux (Fig. 4). Another effect of Zn addition is to significantly reduce undercooling to approximately 4 °C compared to 20 °C for SAC solder. This reduces Ag_3Sn plate size and β-Sn grain size during the soldering [5, 6].

Figure 2(d-f) shows the growth of IMC layers after 1000 h storage at 150 °C. The thickening kinetics of layers of Cu_3Sn, Cu_6Sn_5, and $(Cu,Zn)_6Sn_5$, are analyzed by plotting the average thickness versus the storage time in Fig. 5.

In the SAC/Cu system the Cu_3Sn layer grows at the expense of Cu_6Sn_5 and the Cu_6Sn_5 IMC becomes smoother. In the SAC–1Zn/Cu systems the Cu_3Sn IMC layer appears after a delay



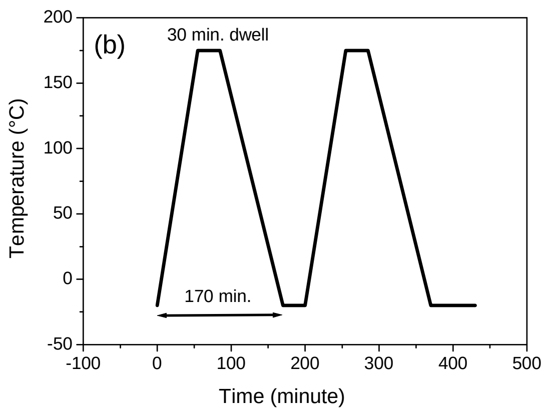


Fig. 1 a) Temperature vs. time graph for solder reflow and b) Temperature cycling profile.

After ageing and thermal cycling experiments, samples were then sectioned and polished with SiC papers and 3 μm and 0.25 μm diamond suspension solution, and examined under optical microscope and a scanning electron microscope (SEM) in combination with an energy dispersive X-ray (EDX) spectrometer to identify phase composition.

3. Results and Discussion

3.1 Ageing

Fig. 2 and Fig. 3 are typical cross-sectional SEM images of the standard interfacial reaction and IMCs formed between SAC and SAC-Zn solder pastes with Cu and Ni(P) substrate during reflow and after ageing. With SAC solder, Cu or Ni diffuses rapidly into the molten solder and forms Cu_6Sn_5 and $(Cu,Ni)_6Sn_5$ IMC on Cu and Ni(P) substrate, respectively. The Zn based solders similarly form $(Cu,Zn)_6Sn_5$ and $(Cu,Ni,Zn)_6Sn_5$ IMCs; the Zn concentration in the interfacial IMC and the type of IMC is strongly dependent on the

of 200 h in high temperature storage. In this system the Cu_3Sn IMC layer only grew to a maximum of approximately 2μm even after 1000 h. In the SAC/Cu system the Cu_3Sn IMC layer becomes rougher after high temperature ageing and the Kirkendall voids that are observed at the Cu_3Sn/Cu interface coalesce into voids and eventually into the crack in Fig. 2d. However, these appear to have been totally suppressed by the addition of 1.5 wt.% Zn in the solder.

The growth rate of the IMC on Ni(P) substrate was slow compared to the IMC growth on Cu substrate, due to the slower dissolution rate of Ni into liquid Sn. Fig. 3c and Fig. 3d shows cross-section SEM micrographs of the SAC/Ni(P) and SAC–1.5Zn/Ni(P) system aged at 150 °C for 1000 h. The presence of Ni_5Zn_{21} IMC grains is also more visible at the interface after ageing. IMC growth is almost negligible due to IMC spalling even after 500h of high temperature storage (Fig. 5b).

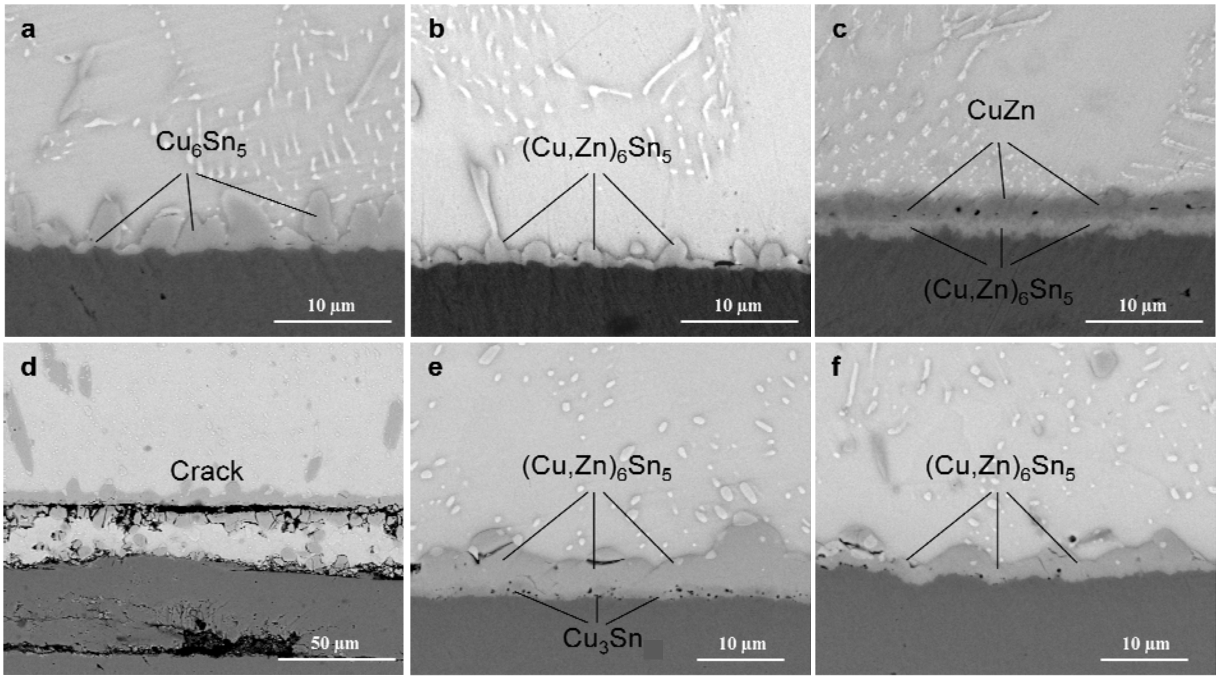


Fig. 2. SEM images showing the interfacial microstructures for: (a) and (d) SAC/Cu; (b) and (e) SAC-1Zn/Cu; (c) and (f) SAC-1.5Zn/Cu, where (a)-(c) as-reflowed and (d)-(f) after high temperature storage at 150°C, 1000 h.

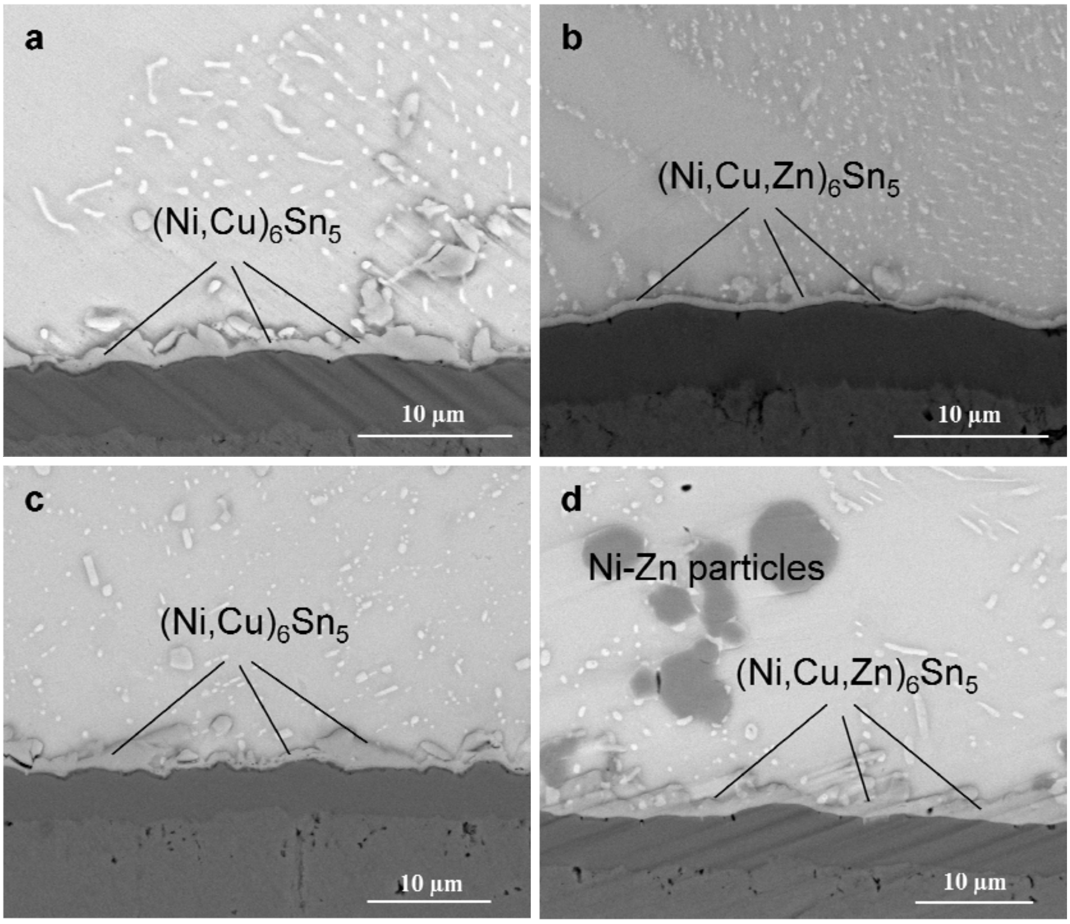


Fig. 3. SEM images showing interfacial microstructures for: (a) and (c) SAC/Ni(P); (b) and (d) SAC-1.5Zn/Ni(P), where the top row images are as-reflowed and bottom row after high temperature storage at 150°C, 1000 h.

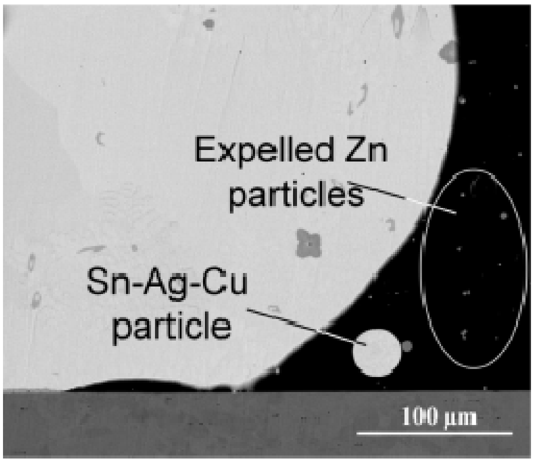


Fig. 4. SEM images of SAC–1.5Zn/Cu system prepared using SAC and Zn powders, showing expelled Zn particles in the flux.

In addition to ageing at 150 °C with solder pastes, ageing at 185 °C was carried out on the same Cu and ENIG substrates using solder ingots of SAC and SAC-1Zn composition. On Cu substrate, the SAC solder exhibited cracks after 200 h while in the SAC-1Zn system the IMC layer grew to 13 µm thickness after 1000 h as seen in Fig.6.

On Ni substrate however, IMC growth remained suppressed in the SAC-1Zn/Ni(P) system and stabilized at 5 µm. These results are shown in Fig.7-8.

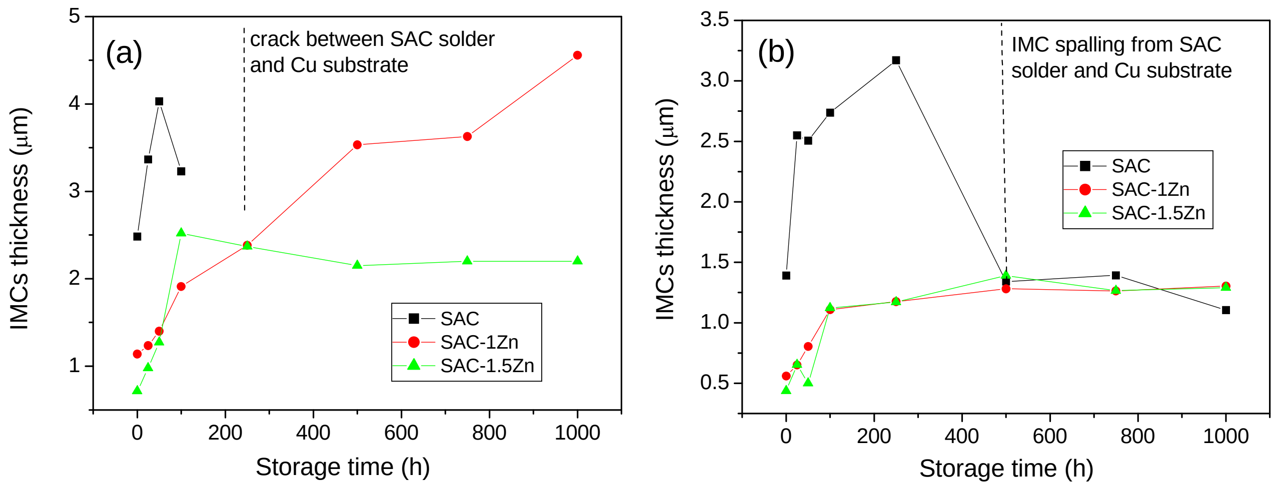


Fig. 5. Plots of mean IMC thickness versus storage time (a) on Cu substrate and (b) Ni (P) substrate.

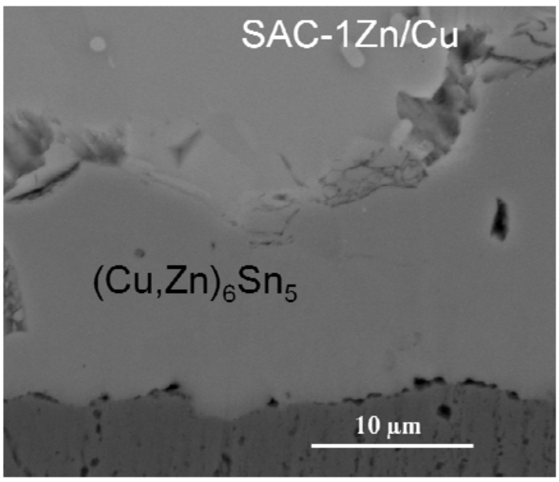


Fig. 6. SAC-1Zn/Cu aged at 185 °C for 1000 h

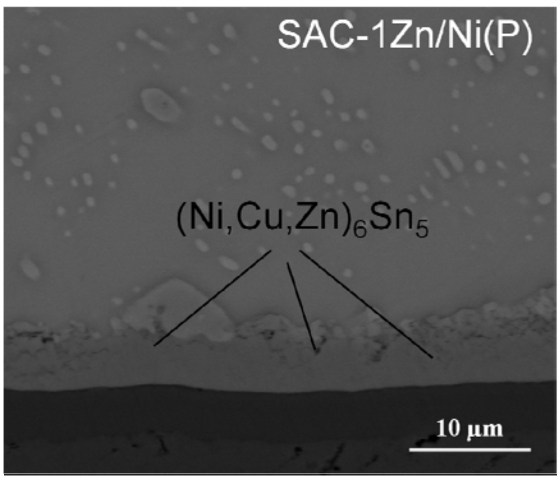


Fig.7 SAC-1Zn/Ni(P) aged at 185 °C for 1000 h

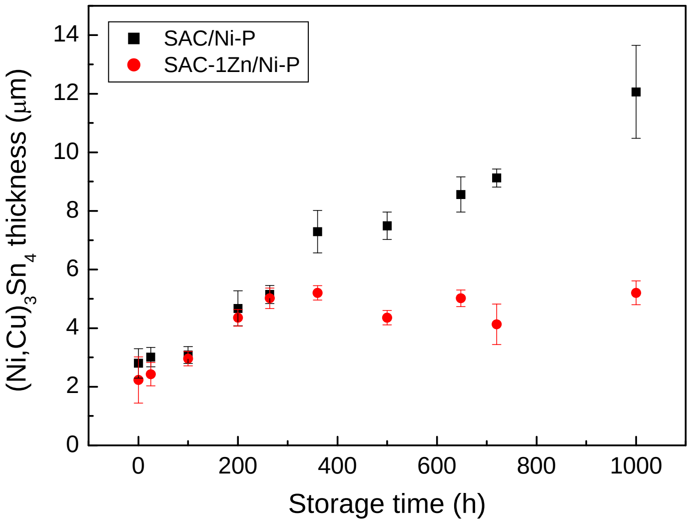


Fig. 8. IMC thickness vs. Storage time at 185 °C for Ni(P) substrate

The assemblies were subsequently aged at 150 °C for 750 h and 1600 h and shear tested using a Dage shear bonder (shear tests performed at ITRI Innovation Ltd., UK). The assemblies were then further aged up to a total of 2000 h and cross sectioned. Table 1 shows the results of the shear tests for large and small resistors, with two repeats for each condition.

For the larger 0603 resistors and SAC-1.5Zn solder no degradation of shear strength is seen after 1600 h while for the smaller 0402 resistor case some initial degradation is seen at 750 h but this stabilizes and no further degradation is seen thereafter. Images of the solder joints after 2000 h at 150 °C are shown in Fig. 9 showing that the SAC-Zn pastes have suppressed IMC growth. Fig.10 shows equivalent results for solder paste printed onto FR4 without components being placed so that only the solder-Cu interface is present and again it is clear that IMC growth has been heavily suppressed by the Zn.

Table 1. Shear strength of resistors after ageing at 150 °C

Solder Type	SAC (0H)	SAC (750H)	SAC +1.5ZN (0H)	SAC +1.5ZN (750H)	SAC +1.5ZN (1600H)
0603 resistors	5.029	4.624	5.654	5.016	5.814
	5.628	4.789	4.842	5.405	4.901
0402 resistors	3.707	2.211	5.824	3.557	3.675
	4.316	2.247	4.978	3.057	3.363

3.2 Shear testing of assemblies after ageing

SAC, SAC-1Zn and SAC-1.5Zn solder pastes were printed onto Cu pads of FR4 PCBs and resistors with Ni terminations were placed and reflowed.

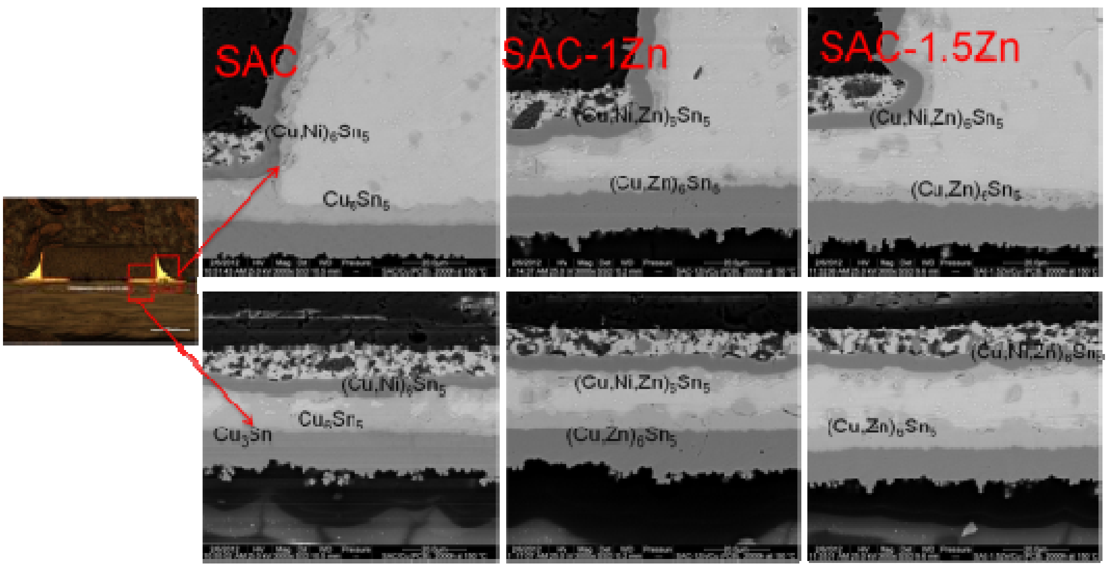


Fig. 9. Cross sections from solder fillet (top row) and under resistor (bottom row) for SAC, SAC-1Zn and SAC-1.5Zn solder pastes after ageing at 150 °C for 2000h.

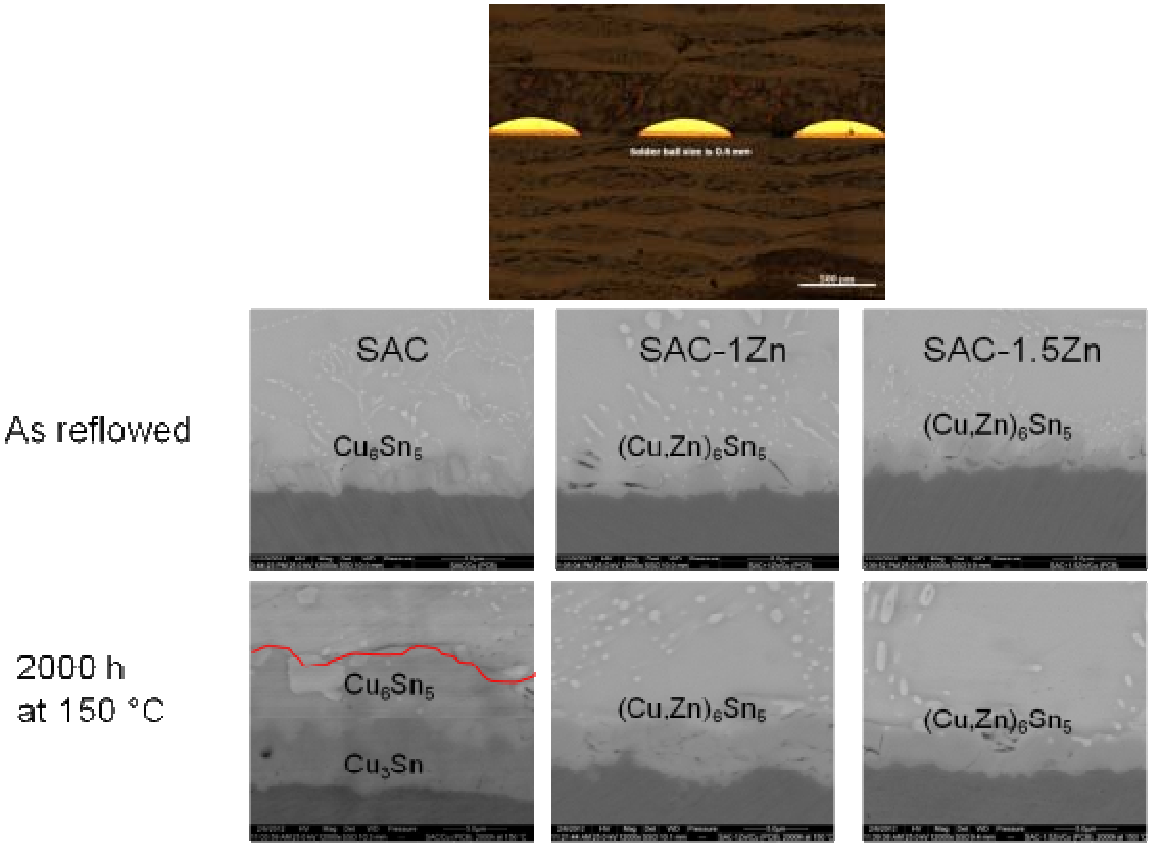


Fig. 10. Cross sections from solder ball for SAC, SAC-1Zn and SAC-1.5Zn solder pastes after reflow (top row) and after ageing at 150 °C for 2000h.

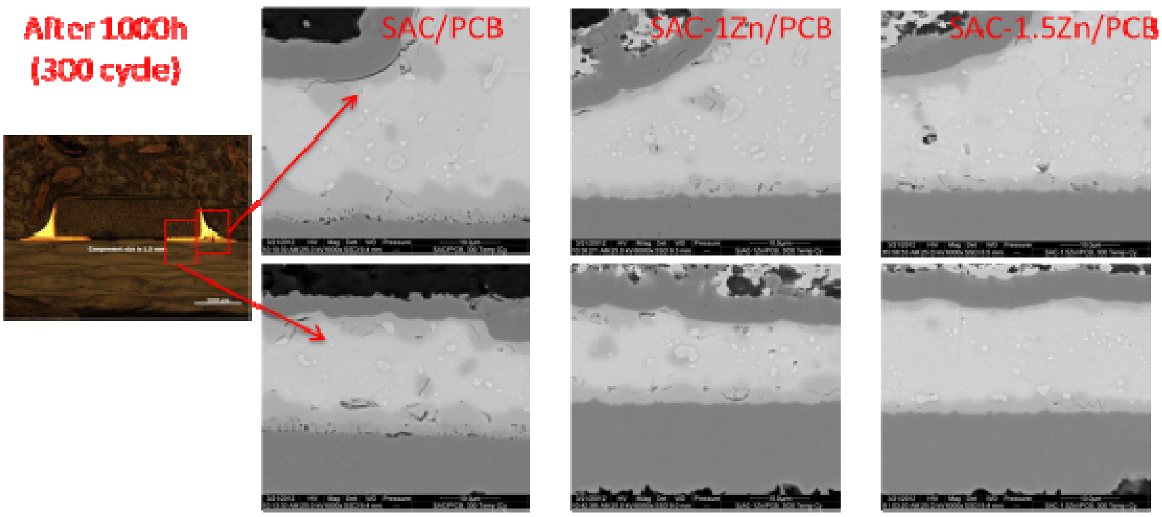


Fig. 11. Cross sections from solder fillet (top row) and under resistor (bottom row) for SAC, SAC-1Zn and SAC-1.5Zn solder pastes after 300 thermal cycles.

3.3 **Temperature cycling**

Temperature cycling experiments were performed on the assemblies described in section 3.2 from -20 to +175°C for 300 cycles (1000 h) cycles. SEM images of cross sections are given in Fig. 11. On the PCB side Cu_6Sn_5 or $(Cu,Zn)_6Sn_5$ forms while on the component side $(Ni,Cu)_6Sn_5$ or $(Cu,Ni,Zn)_6Sn_5$ IMC forms, depending on the presence of Zn in the solder. However, the Cu_3Sn layer and associated Kirkendaal voids were only visible for the SAC solder.

4. Conclusions

Based on the experimental results the following conclusions can be drawn:

- SAC-1Zn forms $(Cu,Zn)_6Sn_5$ interfacial IMC with Cu substrate. SAC-1.5Zn forms a CuZn IMC layer followed by massive spalling. On Ni–P substrate SAC–Zn solder alloys form $(Cu,Ni,Zn)_6Sn_5$ IMC instead of $(Cu,Ni)_6Sn_5$.
- During high temperature ageing at 150 °C on Cu substrate, with SAC–Zn solders $(Cu,Zn)_6Sn_5$ and Cu_3Sn IMCs layers were suppressed significantly compared to the Cu_6Sn_5 layer formed with SAC solder. The IMC growth is suppressed further with SAC-1.5Zn than with SAC-1Zn. During ageing at 185 °C the SAC-1Zn system exhibits high IMC growth after 1000 h though the growth is significantly suppressed compared to pure SAC solder.
- During high temperature ageing at 150 °C on Ni(P) substrate, with SAC-Zn solders the $(Cu,Ni,Zn)_6Sn_5$ IMC growth rate is significantly suppressed and even at 185 °C for 1000 h IMC growth is limited to 5 μm.
- Ageing of assemblies at 150 °C showed significant reduction of IMC buildup after 1000 h on both Ni component terminations and Cu bond pads for SAC-Zn solders compared to SAC solder. Shear testing of the assemblies produced mixed results with shear strength reduced in some cases for SAC-Zn solders compared to strength before ageing. However, further testing showed no further deterioration of strength.
- Overall the SAC-1.5Zn solder shows potential for reliable operation at operating temperatures up to 185 °C, and it is anticipated that Ni bondpads and Ni terminations would produce better results than mixed Cu and Ni metallizations.

Acknowledgments

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