

High temperature solders containing Aluminum and Zinc

H.R. Kotadia, O. Mokhtari, M. Bottrill, M. P. Clode, M. A. Green, S. H. Mannan

Materials Research Group

Division of Engineering and Physics, King's College London, London WC2R 2LS, UK.

Abstract

In this study, we will consider the effect of adding 1-1.5wt.% of Al and Zn to SAC alloy solders in order to limit IMC growth between the solder and the contact metallization. The Al and Zn react strongly with the surfaces on the electronic component and the substrate metallizations that are to be joined. At the solder joint interface, the IMC layer continues to grow at high temperatures and, being brittle, becomes the weakest link in the solder joint. In present work, the interfacial reaction studies were carried out on Cu and Ni(P) substrates. The resultant solder joint microstructure after reflow and isothermal aging at 150 °C up to 500h were investigated under scanning electron microscopy (SEM) with energy-dispersive x-ray analysis (EDX) for phase identification and optical microscopy (OM) for qualitative and quantitative analysis. Our experimental results have confirmed that addition of Al and Zn alloys forms Al-Cu and Cu-Zn on Cu substrate and Al-Ni on Ni(P) substrate respectively. In addition, results have confirmed that addition of Zn alloys plays a crucial role in the composition of IMCs. Addition of Zn (>1wt.%) into basic SAC solder alloy, leads to massive spalling on Cu substrate during reaction. It has been found that additions of Zn into SAC solder alloy can significantly suppress the IMC growth during the aging treatment.

Keywords: Pb-free solder; Intermetallic; Interfacial reactions; Sn-Ag-Cu alloys.

1. Introduction

Solder joints play important roles in electronic packages, which provide electronic connections between components and as mechanical support for the devices [1]. However, conventional electronic connection materials and, in particular, solder joints are not generally reliable at temperatures above 125 °C [2,3]. This is due to the fact that the formation of an intermetallic compound (IMC) layer between the barrier metal and the molten solder is generally necessary to achieve an adhesive bond and hence to ensure electrical conduction, but excessive IMC formation may cause brittle failure. Extensive research has been performed on the interfacial reaction between Pb-free solders and various surface finish layers (Cu and Ni(P) (ENIG-electroless Nickel-immersion Gold)) during reflow and aging [1-6].

When molten Sn-based solder alloy wets the Cu and Ni(P) pad, the formation of Cu-Sn and Ni-Sn IMC layers are desirable. However continued growth in the solid state especially at high temperatures, degrades the long-term reliability of the solder joint. Traditionally trace amounts of certain elements i.e. rare earth elements, have proven to be effective in suppressing the growth of Cu-Sn IMC layers and consequently improved long term reliability of the solder joint [7]. Recently, several researchers [6,8,9] have demonstrated that addition of small quantities of Al or Zn suppress Cu-Sn IMC layer growth. The addition of these elements into the solder paste and subsequent reflow soldering in such a manner as to avoid oxidation [7] and non-wetting during soldering is the subject of ongoing research, and is not explicitly addressed in this paper.

This study focused on the interfacial reaction between Sn-3.8wt.%Ag-0.7wt.%Cu (SAC) solder alloy with varying amounts of Al and Zn addition on two different substrates; Cu and Ni(P) during reflow and aging at 150 °C for 500h. It has been found that addition of Zn into SAC solder alloy can significantly depress the IMC growth and change the various IMC phases that form. The addition of the Al into SAC solder alloy results in formation of an Al-Cu IMC in the solder matrix. Massive spalling is observed in the SAC-1.5Zn/Cu and SAC-Al/Ni(P) systems.

2. Experimental procedures

Sn-3.5Ag-0.7Cu (SAC) solder alloy was supplied by Henkel Ltd, UK. Predetermined quantities of SAC ingots and Al foil were mechanically compressed and placed in a quartz tube sealed into

an electric resistance furnace with vacuum (10^{-5} Torr vacuum) and those with Zn alloys were prepared in an electrical resistance furnace in air. All compositions in this article are given in weight percent unless otherwise stated.

Ni(P) substrates supplied by Schlumberger, consisted of Electroless Ni immersion gold bond pads on polyimide boards. The Cu substrates consisted of Cu coated FR4. Both Ni(P) and Cu substrates were cut into square plates (~5 mm) with metal thickness of ~40 µm. Before reflow, the substrate was cleaned using IPA, acetone, and finally deionised water. For all the alloys 0.100 ± 0.002 g mass of the solder alloy was coated by a thin layer of flux, and placed onto the Cu and Ni(P) substrate with a solder layer approximately 1.5 mm thick (maximum) and placed into a reflow oven. The reflow was carried out in air: preheating at 140 °C for 150s and soldering at 260 °C for 60s. The resulting solder had a maximum thickness of 1 mm at the top of the solder dome. Aging was carried out in air at 150 °C for between 1 to 500h. After reflow and aging, the samples were cross-sectioned and polished with SiC abrasive papers and 0.25-µm diamond suspension solution.

The microstructures were observed without etching under a ZEISS Axioscop2 MAT optical microscope equipped with an automated Zeiss AxioVision image analyzer, which was used for the microstructural investigation and quantitative analysis. An FEI scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDX) at an accelerating voltage of 25 kV was used to achieve higher magnification in areas of interest, as well as to quantitatively identify each phase region.

3. Results and Discussion

Fig. 1a is a typical cross-sectional SEM image and EDX analysis revealed that the interfacial reaction between SAC/Cu and SAC/Ni(P) substrate forms intermetallic compounds (IMCs) during reflow. Cu and Ni diffused quickly into the liquidus state of the solder to form Cu_6Sn_5 and $(\text{Ni,Cu})_3\text{Sn}_4$ with a scallop-type IMC morphology. In addition, the SAC solder alloy has a structure of Sn-rich grains (β -Sn) with some Ag_3Sn and Cu_6Sn_5 phase precipitates above the interfacial IMC. In this study, the microstructure and interfacial reaction of SAC solder alloy was studied as Zn and Al content is varied (e.g. Fig. 2). For understanding the effects of Zn and Al addition on the microstructure modification, careful observation and examination carried out by EDX analysis to detect possible

segregation of Zn and Al atoms during interfacial reactions of solder on Cu and Ni(P) substrates.

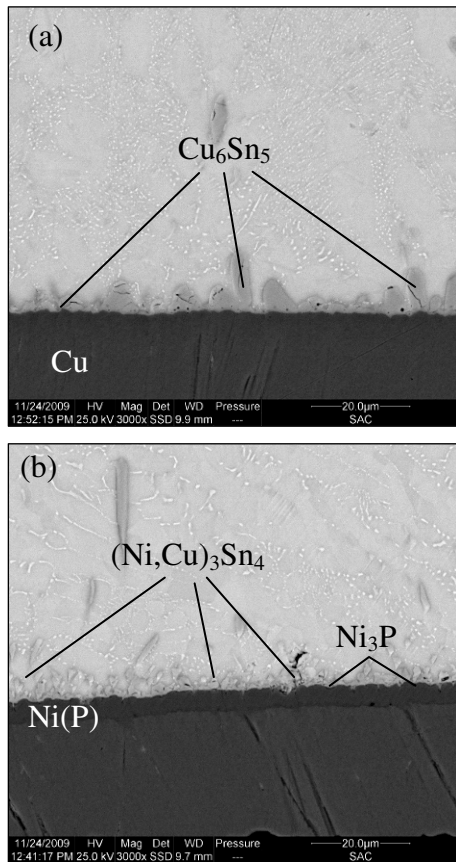


Fig. 1. SEM Backscattered electron micrographs illustrating the SAC solder alloy on (a) Cu and (b) Ni(P) substrate, after reflow.

The IMCs formed on the interface and solder matrix strongly depend on the amount of Zn wt.% addition into the basic SAC solder alloy. On Cu substrate, immediately after reflow (260 °C for 60s), 0.5-1wt.%Zn addition made only slight differences to IMC cross section microstructure, and Cu_6Sn_5 IMC formed at the solder/Cu interface (Figs. 2a and b). By contrast, addition of 1.5wt.% Zn modified the interfacial IMC formation, which shows massive spalling at the interface (Fig. 2c), just after reflow. This phenomena has previously been observed between a Sn-based solder and Ni(P) interface, particularly when the solder joint is subjected to cyclic stresses, as thermally activated diffusion in the solder material, metallization and IMC may take place [10]. Two IMC layers were identified at the interface; a Cu_6Sn_5 IMC adjacent to the Cu substrate and a Cu-Zn based compound in the solder itself, while the gap between the Cu-Zn and Cu_6Sn_5 layers was occupied by solder. Such spalling was attributed to the possibility that the original reaction product at the interface is no longer in local thermodynamic equilibrium with the solder, and this compound is driven away to make

room for the nucleation and growth of the equilibrium phase [1]. The IMC phase that nucleates first during the soldering processes at the interface is dependent on the driving force of formation and interface energy. In contrast to the SAC-1.5Zn/Cu interface, the SAC-1.5Zn/Ni(P) interface does not show any sign of massive spalling, as shown in Fig. 5c. Fig. 3, delineates the elemental distribution after reflow at 260 °C for 60s. It is seen that Zn segregates at the SAC-1Zn/Cu and SAC-1.5Zn/Cu interfaces. The analysis line passes through the compound layer and shows an overlap of Cu and Zn in the SAC-1.5Zn/Cu system, indicating Cu_5Zn_8 IMC formation. It is thus clear that addition of 1 and 1.5 wt.% Zn causes the formation of an IMC while at 0.5% no IMC layer or particles form.

During the process of thermal aging, IMCs grow continuously due to elemental diffusion, resulting in morphology change and thickness increase. In industrial practice, these solder joints may experience temperature cycles from -40 °C to 150 °C, or higher [6]. Thermal energy drives IMC growth, and ductile solder is progressively converted into brittle IMCs, so that less deformation can be accommodated by solder joint. A comparison of the average IMC thickness and the morphology on the interface were performed during isothermal aging at 150 °C for 500h. The IMC thickness versus the aging time of samples was plotted in Fig. 4. The interesting result was that at the SAC-Zn/Cu interface, the Cu_3Sn IMC layer only grew to approximately 1 µm after 500h of high temperature aging at 150 °C. As is well known, the suppression of the Cu_3Sn would then be expected to improve mechanical and electromigration reliability [11].

It is evident from Fig. 5 that the morphology of the $(\text{Ni,Cu})_3\text{Sn}_4$ IMC on SAC-Zn/NiP changes in comparison to the SAC/Ni(P) as-reflowed sample. The interfacial intermetallic becomes progressively more planar as the Zn content is increased. On the Ni(P) substrate during the soldering the consumption of the Ni at the edge of the solder joint was higher compared to the centre of the solder interface which can explain by the larger difference in thermal expansion mismatch [10]. During the process of thermal aging, $(\text{Ni,Cu})_3\text{Sn}_4$ IMC grows continuously but less rapidly compared to the Cu-Sn IMC. According to the diffusivity data, Ni has a lower diffusion coefficient in Sn compared with Cu [12]. However, these interfacial IMCs are further suppressed by addition of Zn. Fig. 6 shows element distribution on the Ni(P) substrate. Result clearly indicate a small level of interaction between Ni and Zn, but there is no direct evidence of a new

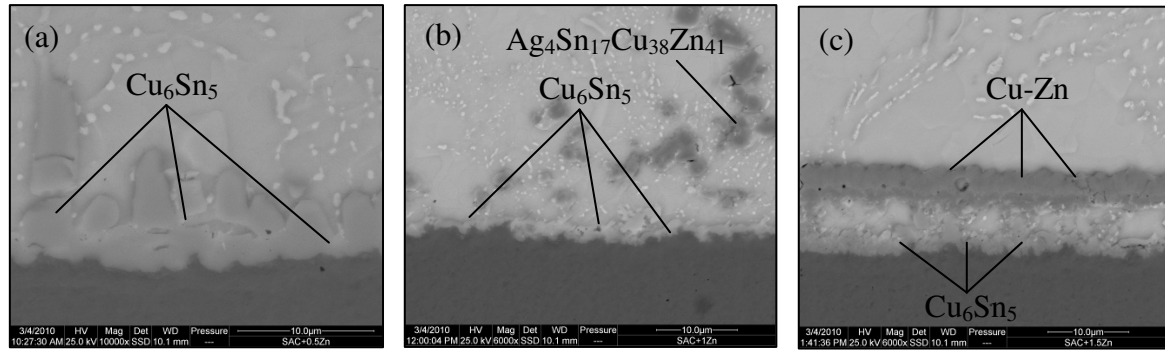


Fig. 2. SEM Backscattered electron micrographs illustrating the (a) SAC-0.5Zn (b) SAC-1Zn and (c) SAC-1.5Zn solder alloys on Cu substrate after reflow.

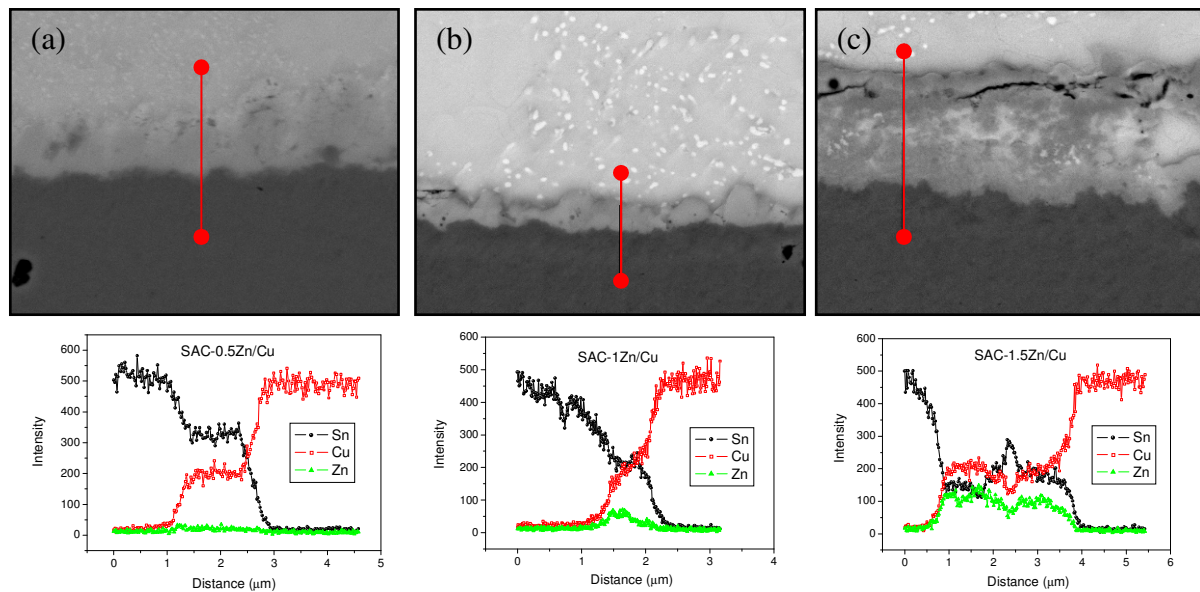


Fig. 3. Elemental analysis of (a) SAC-0.5Zn, (b) SAC-1Zn, and (c) SAC-1.5Zn solder alloys on Cu substrate, after reflow.

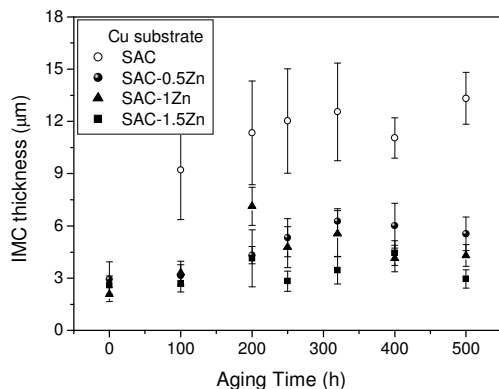


Fig. 4. Intermetallic compound (IMC) thickness as function of aging time on Cu substrate.

(Ni,Zn)₃Sn₄ IMC forming. The IMC thickness versus the aging time of Ni(P) samples graph plotted in Fig. 7.

At low concentrations of added Al, the Al formed two distinct types of Al-Cu and Al-Ag IMC particles in the solder matrix. SAC-Al solder alloy reacts with Cu and Ni(P) substrate and forms Al₂Cu and Al₃Ni IMC. Once the Al has reacted to form an IMC layer between the solder and the joining surfaces, this IMC layer remains unstable. After increasing the Al wt.% in the solder, Al₂Cu and Al₃Ni particle concentration significantly increases, mostly due to the reaction with Cu and Ni dissolved from the substrate. Based on the current experimental evidence it is believed that the large Al₂Cu particles grow during the first reaction of Al with the Cu substrate and that later, these Al₂Cu particles are pushed away by Sn-rich dendrites, which grow upwards from the substrate during

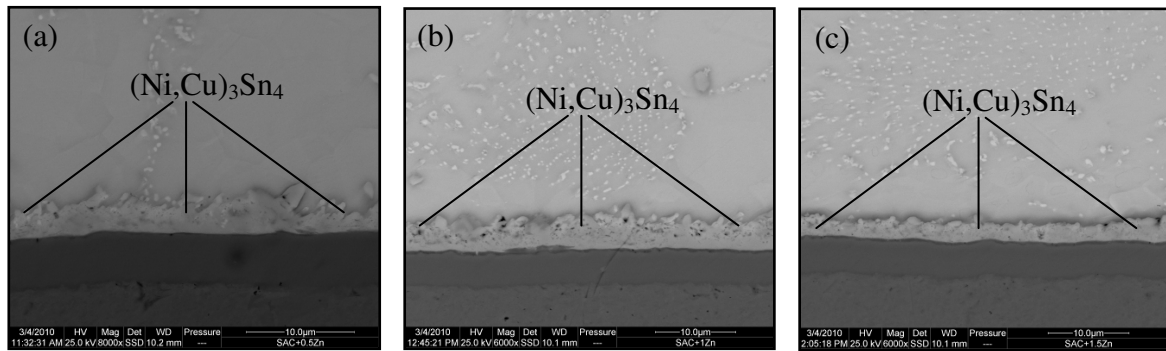


Fig. 5. SEM Backscattered electron micrographs illustrating the (a) SAC-0.5Zn (b) SAC-1Zn and (c) SAC-1.5Zn solder alloys on Ni(P) substrate after reflow.

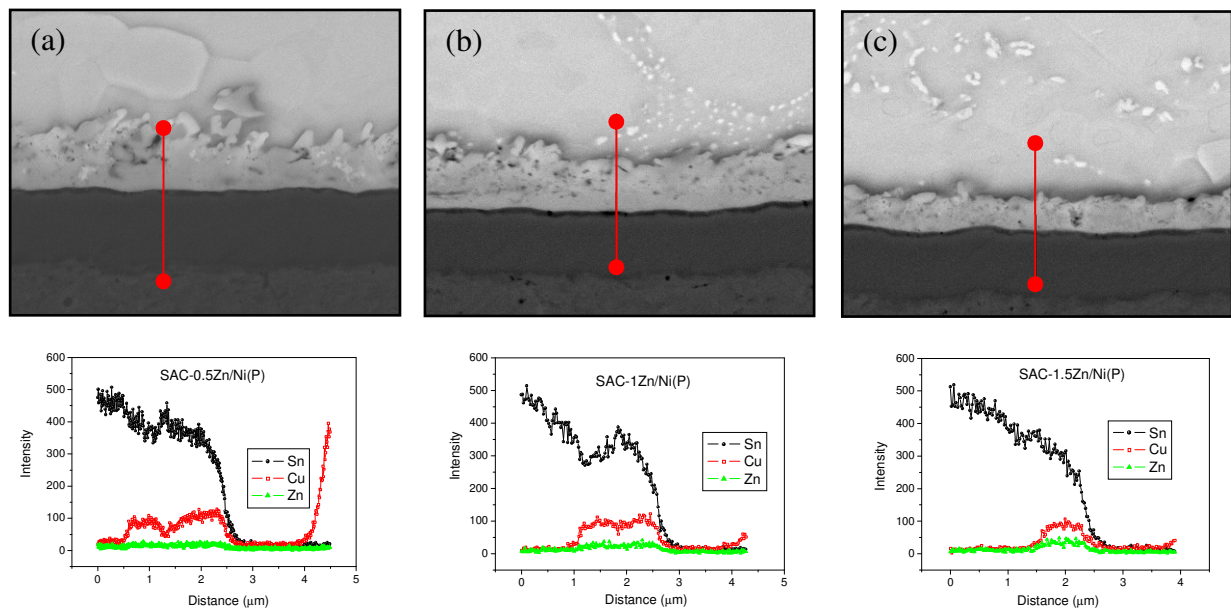


Fig. 6. Elemental analysis of (a) SAC-0.5Zn, (b) SAC-1Zn, and (c) SAC-1.5Zn solder alloys on Ni(P) substrate, after reflow.

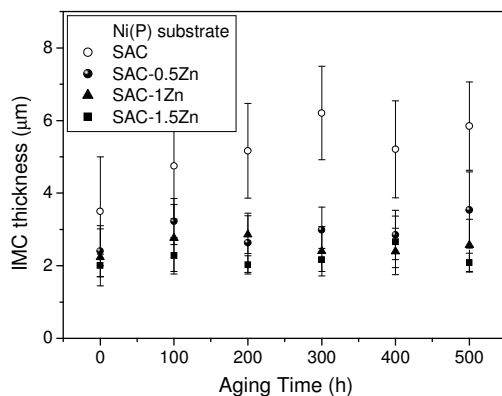


Fig. 7. Intermetallic compound (IMC) thickness as function of aging time on Ni(P) substrate.

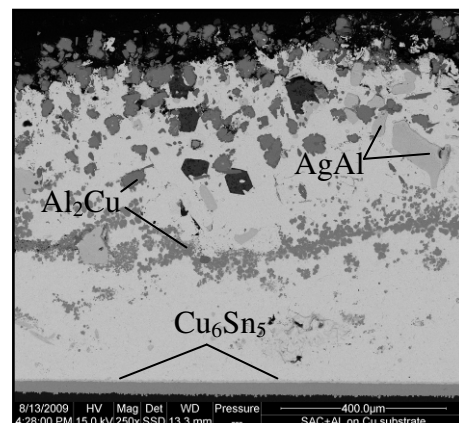


Fig. 8. SEM Backscattered electron micrographs illustrating the SAC-1Al solder alloy on Cu substrate.

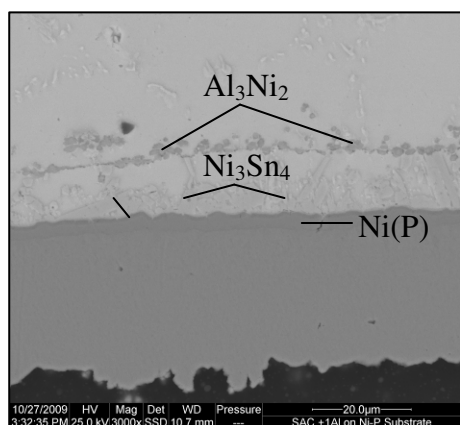


Fig. 9. SEM Backscattered electron micrographs illustrating the SAC-1Al solder alloy on Ni(P) substrate.

solidification (Fig. 8). However, small particles are trapped inside the dendritic arms. In contrast to the SAC-Al/Cu interface, the SAC-Al/Ni(P) interface does not show any Al_3Ni_2 segregation on the solder surface. The Al_3Ni_2 IMC layer forms about $\sim 5 \mu\text{m}$ from the Ni(P) substrate (Fig. 9). From the our preliminary experiment evidence it is believe that this Al_3Ni_2 IMC nucleates at the solder/Ni(P) interface and after consumption of the Al atom from the solder Al_3Ni_2 IMC spalls from the substrate and most stable $(\text{Ni,Cu})_3\text{Sn}_4$ phase nucleate at the interface. However, more studies are needed to understand the role of Al alloying element on Sn-based solder alloy.

4. Conclusions

The Zn alloying element plays a crucial role on the Cu and Ni(P) interfacial reaction. The IMCs formed on the interface are strongly dependent on the amount of Zn added into the basic SAC solder alloy. In the case of Zn concentration of between 0-1 wt.% added to the solder alloy, a Cu_6Sn_5 IMC layer forms at the interface. Increasing concentration of Zn to 1.5 wt.% results in Cu_5Zn_8 and Cu_6Sn_5 IMC layers at the interface, with massive spalling of the Cu_5Zn_8 . This is interpreted as follows: the first reaction product at the interface of SAC-1.5/Cu system is Cu-Zn IMC, which is not in thermodynamic equilibrium with the solder after consumption of Zn atom from the solder matrix and this compound allows the nucleation of the more thermodynamically stable phase (Cu_6Sn_5) in later stages of interface growth. In the SAC-Zn/Ni(P) system, this massive spalling effect is not seen and at the interface $(\text{Ni,Cu})_3\text{Sn}_4$ IMC forms in all three alloys. However, Zn significantly suppresses the Cu_6Sn_5 and Cu_3Sn IMC growth during aging at 150°C up to 500h in both Cu and Ni(P) substrate.

The addition of Al in SAC solder alloys does not change the IMCs formed at the substrate. Al from the solder reacts with Cu from the substrate to form Al_2Cu intermetallics, which are segregated away from the substrate during the solidification. In case of Ni(P) substrate the Al_3Ni IMC layer formed about $\sim 5 \mu\text{m}$ from Ni(P) substrate, rather than at the substrate interface forming a barrier layer, in contrast to ref. [9] where the experiments were carried out in a solder bath rather than with limited volumes of solder.

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