The Study of Interfacial Reaction between SnAgCu (SAC) Lead-free Solder Alloys and Copper Substrate: A Short Review

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Abstract. This paper is aimed to review and study the interfacial reaction between SnAgCu (SAC) lead-free solder alloys and common copper substrates. Among the lead-free solders, a ternary solder alloys, SnAgCu (SAC) based solder, is leading the lead-free solders as it has excellent thermal and electrical properties. The interfacial between solder alloy and substrate comprise an important characteristic in the reliability performance of a solder alloy. As the current industry has driven to miniaturization, high integration and multifunctionality, the reliability and durability of solder joints are gained attention for its long-term performance of electronic products. Therefore, in this short review, the interfacial reaction between SAC solder alloys and copper substrate will be focused. Besides, the effects of the addition of microalloying elements into SAC solder alloys will be discussed.

1. Introduction

The process that joining two or more electronic components together by using the metallic alloys is known as soldering. It is an important process in the manufacturing of electronic devices, where solder act as the interconnection in electronic assemblies. Solder should require the properties like electrical, thermal conductive and good mechanical properties in an electronic circuit. The traditional eutectic Sn-Pb alloys are the dominant solder materials in the field of electronic packaging. However, for the sake of environmental protection, the restriction of Hazardous Substances (RoHS) has enforced a law to ban the use of Pb in electronic industry since the year 2006 [1]. Consequently, it has brought up a great effect on developing lead-free solder alloys.

Many researchers have been proposed alternative lead-free solder to take over the traditional eutectic Sn-Pb solder alloys [1-4]. Many of the alternatives solder alloys are made by Sn-based solders and usually alloyed with Ag, Bi, Au, Cu, and In. Amongst these lead-free choices, a ternary eutectic composition has emerged for broad use across the electronic industries, which is SnAgCu (SAC). This is because SAC solder alloys have excellent wettability and great mechanical characteristic [5, 6]. However, the most ideal chemical composition for the eutectic reaction is still under debate. Although SAC solder alloys are chosen as the suitable candidate in place of Sn-Pb alloys, it faces some challenges in the development. For instance, the formation of undesirable intermetallic compounds (IMC), like Ag3Sn is the major challenge of SAC solder alloys.

To overcome this problem, many researchers have been proposed as an alternative approach, which is microalloying with the fourth element. The fourth element could be rare-earth elements, transition, and post-transition metals [7-13]. For example, Mg, Al, Ce, Zn, Fe, and Ge have been proposed by
several researchers. Yet, the formation of new intermetallic was observed after microalloying. These new intermetallic enhance the solder performance is controversial. Some researchers claim that these newly formed IMC would help to suppress the formation of Ag$_3$Sn. The Ag$_3$Sn is suppressed by controlling the undercooling at low solidification rates with the addition of alloying elements.

Furthermore, the intermetallic layer will be formed at the interface as there are some reactions take place between solder alloys and copper substrate. This intermetallic layer comprises a crucial character in the manufacturing and reliability of a solder alloy [14]. Therefore, several researchers have a great interest in the formation and growth of the interfacial intermetallic layer between solder alloys and copper substrate. Hence, the aim here is to review and summarize the properties of SAC solder alloys after the addition of the microalloying element.

2. Results and Discussion

2.1. Interfacial reaction
As mentioned previously, the intermetallic layer is important in the discussion of reliability performance of a solder alloy. A thin layer of IMCs at the interface is reported to be desirable to work out a good metallurgical bonding. On the other hand, excessive growth of intermetallic layer may bring negative impacts to the solder joint as the intermetallic layer behaves brittle characteristic [15]. The common IMCs that will be found in the interfacial between SAC solder alloys and common copper substrate are Cu$_6$Sn$_5$, Cu$_3$Sn and other IMCs. The Cu$_6$Sn$_5$ is the first IMC form at the interface during the soldering process, then, followed by a thin Cu$_3$Sn form between Cu$_6$Sn$_5$ and copper substrate by solid-stage reaction [16].

![Figure 1. The interface between Sn3.8Ag0.7Cu solder alloy and copper substrate. Cu$_6$Sn$_5$ had a scallop-like structure, Cu$_3$Sn had a more planar structure and some Kirkendall voids present at the Cu$_3$Sn layer [16].](image-url)
Figure 2: The micrographs of (a and c) Sn3.5Ag1.0Cu solder alloys and (b and d) SAC-0.4Zn solder alloys before (a and b) and after 600hr aged at 150°C [9].

Figure 2 represents the scanning electron microscope (SEM) micrographs of Sn3.5Ag1.0Cu solder alloys with Zn addition [9]. As can be seen in figure 2, the scallop-like structure Cu$_6$Sn$_5$ presented (a and b), and it changed to a more planar structure (c and d) after 600hr aged at 150°C. The transformation of intermetallic layers may be caused by the change in interfacial energy. The interfacial energy between solid solder and Cu$_6$Sn$_5$ is high and it leads the compound changes to a flatter surface layer type during aging process. However, the growth of the scallop-like structure is due to the rapid gain in compound formation energy that may compensate for the surface energy spent during the wetting reaction[17]. The team also found that the intermetallic layers in between Sn2.8Ag0.5Cu-1wt%Bi and copper substrate tend to transform from scallop-like structure to planar structure after the aging process.

Meanwhile, as the aging time is increased, the thickness of the Cu$_6$Sn$_5$ and the Cu$_3$Sn IMC layers increase. The Cu$_6$Sn$_5$ IMC become more significant as the aging time extended. The formation of Cu$_6$Sn$_5$ before Cu$_3$Sn is because of Cu$_6$Sn$_5$ IMC has lower activation energy, and it is thermodynamically unstable. Hence, the Cu$_3$Sn layer is formed by consuming the Cu$_6$Sn$_5$ layer [18]. Furthermore, the growth of Cu$_6$Sn$_5$ and Cu$_3$Sn IMCs layer is retarded with the addition of Zn. The mechanism of the retardation of the IMCs layer is not be explained [9], but other researchers have mentioned the addition of the fourth element to SAC solder alloy leads to the formation of new intermetallic. The newly formed intermetallic has the tendency to reduce the ability of Cu-Sn IMC to be formed [19, 20]. Researches have been proposed that adding Mn into Sn3.0Ag0.5Cu and Sn0.3Ag0.7Cu solders respectively also can help to suppress the growth of the IMCs layer [21,22].

Also, Ag$_3$Sn IMC was observed spread uniformly within the solder after the reflowing process. The Ag$_3$Sn IMC present in a planar structure near the interface. The presence of this IMC has changed significantly and tends to merge to form a large platelet with increasing aging time [23]. As mentioned before, Ag$_3$Sn IMC is the major challenge of SAC solder alloys as they may cause mechanical failure. Fatigue crack may initiate and propagate along with the interface between Ag$_3$Sn and solder matrix, as there is a high stress concentration area. The interfacial microstructure of low silver content SAC solder alloys, Sn1.0Ag0.5Cu with minor addition of Zn [24]. The results published the Cu$_6$Sn interfacial IMC is suppressed after aging period. These findings are in agreement who added Zn into Sn3.5Ag1.0Cu solder [9].
Collectively, it can be concluded that the addition of minor alloying elements into SAC solder alloy could affect the reaction at the interface between the solid solder and the common copper substrate. These effects can be summarized into 3 majors; Firstly, the addition of microalloying elements could alter the IMC growth rate. Second, the physical properties of the phases formed at the interfacial can be changed, and lastly, an additional reaction layer might be formed at the interface or they will take place of the binary phases that normally exist and form new reaction products instead [14, 20-27].

2.2. Mechanical properties
As it can be seen in figure 3, all the quaternary alloys have a slightly higher UTS value than the ternary Sn-based alloy.

![Figure 3. Ultimate tensile strength (UTS) and elongation of various alloying elements (Ni, Co, and Fe) addition to Sn3.0Ag0.5Cu solder alloy[28].](image)

The effects of fourth alloying elements (Fe, Mn, Ni, Ti, and Co) addition on the tensile properties of Sn3.0Ag0.5Cu [28]. The addition of fourth elements leads to the formation of new precipitate in the solder alloy, thus, result strengthening effect and degradation in ductility. Amongst the fourth elements, Fe showed the highest UTS value but the elongation is lower than Sn3.0Ag0.5Cu. While, when 0.1wt% of Mn and Ni added int SAC solder alloys, the results showed an improvement in the ductility behaviour. An appropriate amount (0.15wt%) of Y addition to Sn3.8Ag0.7Cu solder alloy could effectively enhance the mechanical properties of the solder alloys[29]. The team further explained that Sn atoms are released from forming SnO2, reacted with the Cu atom from the Cu substrate, to form a layer which is beneficial to bonding. Hence, a hypothesis is made that Y promoting the chemical reactions at the bonding interface and provided a durable bonding during the soldering process. An excessive amount of additive addition to SAC solder alloys may lead to the formation of new IMCs, which will tend to degrade the mechanical properties and reliability performance of the solder joints.

The adding rare-earth (RE) elements, such as Ce and La, enhanced the ultimate tensile strength of the Sn3.8Ag0.7Cu solder alloys [30]. While the elongation decreases gradually after the alloying element exceeds 0.25wt%. Reduction in elongation is explained as the presences of the hard RE compounds, the number of RE hard compounds increase as the alloying element content increase. However, these findings are in contrast which is the ultimate shear strength of the Sn3.9Ag0.7Cu solders decreased as the amount of alloying element increase [31]. Whereas, the elongation is higher after the addition of Ce and La as compared to Sn3.9Ag0.7Cu solder alloys. He further explained that the formation of RE compounds gives an impact on the ductility of solder alloys.

3. Summary
As the results presented and discussed above, the importance of the interfacial intermetallic compounds (IMCs) towards the solder joint structure has always been emphasized. The effects of microalloying element addition into the SAC solder alloys on the microstructure transformation can be observed clearly. The changes in microstructure after addition of microalloying elements is due to the IMC reaction/ IMC growth rate changes. Nevertheless, new reaction layer or new compounds may form at
the interface. These new compounds tend to disturb the elongation of the solder alloys, and hence it will affect the mechanical strength of the solder joints. However, not all microalloying element is suitable for enhancing the properties of SAC solder alloys. Therefore, further research and attempts could be done by adding various microalloying elements into difference composition of SAC solder alloys.

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