The effect of Aluminium addition on the microstructure of lead-free solder alloys: A short review

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Abstract. The ban on using lead in electronic packaging has been taken effect since the year 2006. The alternative to replacing lead (Pb) based solder has been given highly concerns by the electronic industry. Both Sn-Ag-Cu and Sn-Cu solder alloys were considered to be the most acceptable candidates to replace SnPb solder alloy. From the findings, it showed that β-Sn appears as island-like shape and eutectic phases appear as a darker shade. The grain size is refined significantly after incorporated with a suitable amount of Al. When exorbitant amount of Al addition will cause Al-rich particles, which has high potential to acts as the heterogeneous nucleation site and result in a lower degree of undercooling. The most desired amount of Al addition is between 0.025 - 0.05 wt%. The primary intermetallic compounds found in Sn-based solder alloy are Cu₆Sn₅ and Ag₃Sn. New intermetallic compounds were found after addition of Al, which are Cu-Al and Ag-Al intermetallic. The formation of new intermetallic compounds causes the formation of Cu₆Sn₅ and Ag₃Sn to be suppressed.

Introduction

Soldering is a process of assembling or interconnecting two or more electrical components together with solder alloys. Pb based solder alloy has been used since the earlier Bronze Age [1, 2]. However, the ban of using hazardous materials such as leads, mercury, cadmium for electrical and electronic equipment, has been enforced by The Restriction of Hazardous Substances (RoHS) since the year 2006. Therefore, the development of lead-free solder is given extensive concerns. Amongst the lead-free solder, the near eutectic SnAgCu (SAC) solder alloy is found to be the most satisfied candidate to replace Sn-Pb solder, as Ag and Cu have excellent thermal and electrical properties, which fulfilled the primary requirements of the solder alloys. Currently, Sn-3.0Ag-0.5Cu (SAC305) and Sn-3.8Ag-0.7Cu (SAC387) are mainly used in electronic industries [3-7]. But Ag is costly; hence, some researchers are also working on SnCu solder alloy.

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Although SAC and SnCu solder alloys are compatible with Sn-Pb solder alloy, it has some drawbacks and still facing some challenges at the current stage. For instance, poor wettability, reliability and high melting point, are failed to meet the needs of current industry. Furthermore, the strength of the solder joint of current lead-free solder may degrade after undergoes a reflowing process or expose to external impacts or harsh environment condition [8-11]. This is because brittle fracture may happen as the rapid growth of the interfacial layer on the interfaces. Consequently, many researchers also have been added rare earth elements and metal alloy elements into SAC and SnCu solder alloys in order to achieve better performance and reliability of solder alloys [9, 12-24]. The performances of incorporated solder alloys can be enhanced by controlling the thickness of intermetallic compound (IMC), alter the morphology, prevent phases changes and increase the toughness.

The features that included in microstructure analysis are: (1) grains size, (2) grains boundaries, (3) interfaces, (4) phases precipitation and so on. These features can be altered with respond to surrounding conditions, such as external loads, impacts and temperature [25]. So, these make microstructure as one of the most accurate and direct reliability assessment of solder joint. Also, it enables the development of more reliable solder interconnection. This is why microstructure analysis is important in failure analysis of a material. The Cu₆Sn₅ and Ag₃Sn intermetallic (IMC) can easily be seen in the microstructure of SAC solder alloy. The formation of these IMC are due to the atomic diffusion between Cu substrate and Sn-based solder during the reflow process. Yet, these IMCs are brittle in nature, thus, undesire amount of IMCs can weaken the solder joint reliability. For that reason, researchers found that additional element can suppress the formation of Cu₆Sn₅ and Ag₃Sn by forming another new intermetallic. This paper is aimed to review the effect of Al addition on the microstructure of lead-free solder alloy.

### 2 Effect of Al Addition on the Microstructure

#### 2.1 Effect on SAC solder alloys

Fig 1 shows the microstructure of Sn 3.0Ag 5.0Cu (SAC35) with different amount (0.025 – 0.2wt%) of Al addition. The presence of primary intermetallic dendrites and eutectic phase can be clearly seen in Fig 1. The primary intermetallic dendrites were known as Cu₆Sn₅, which appeared in the darker region, whereas the eutectic phase, the β-Sn appeared in the brighter region. The length of Cu₆Sn₅ was shortened and the growth of secondary dendrite was restricted after the addition of Al into SAC35 solder alloy. The shortest length of Cu₆Sn₅ was found at Al content of 0.025 wt%. When exorbitant (>0.05wt%) of Al added, the intermetallic became slightly longer. Furthermore, the exorbitant of Al addition may causes agglomeration, which has high potential to act as a heterogeneous nucleation site for Cu₆Sn₅ [26]. Al addition has boosted intergranular eutectic nucleation, which resulting in eutectic grain refinement. It is expected that the mechanical strength of a reasonable amount of Al added solder will be better than pure SAC solder, as the grain size is refined and it can impede dislocation motion [16].
Fig 1: SEM micrographs of SAC35 solder alloys with addition of Al at magnification of 40x. (a) 0 wt% Al, (b) 0.025 wt% Al, (c) 0.05 wt% Al, (d) 0.1 wt% Al, and (e) 0.2 wt% Al [27].

In addition, the other intermetallic compounds such as CuAl, CuAl₂, AgAl, and Ag₃Al also can be found in Al added SAC solder alloys. These new IMCs can be seen in Fig 2 and they are more favorable to be formed compared to Cu₆Sn₅ and Ag₃Sn. This is because Cu-Al and Ag-Al IMC have bigger electronegativity [28], thus, they are more likely to be formed instead of Cu₆Sn₅ and Ag₃Sn. However, the CuAl₂ and AgAl are formed only at higher Al content sample. Moreover, Al-Sn-Cu IMC also can be appeared, this IMC is undesirable as it is expected to decrease the shear strength of the solder alloy.

Fig 2: SEM micrographs of SAC0305-2Al bulk solder at a magnification of 1000x [29].

Besides, the addition of Al into SAC solder alloys can suppress the formation of Cu₆Sn₅ also have been proven after reflowed on Cu substrate. As shown in Fig 3, the SAC0305 with 1 wt% Al were showed the thinnest IMC layer as compared with SAC0305 and SAC0305-2 wt% Al. The Cu₆Sn₅ layer appears in scalloped shaped, which is formed by diffusion process between solder alloy and Cu substrate [30].
2.2 Effect on SnCu solder alloys

Fig 4 reveals the optical microstructure of Sn-0.7Cu and Sn0.7Cu with different amount of Al addition (0.01 – 0.075wt%). Same as Al addition in SAC solder alloy, the β-Sn and primary intermetallic Cu₆Sn₅ phases can be found in the samples. From the findings, the microstructure of β-Sn and Cu₆Sn₅ are refined and the size becomes more uniform [31]. A similar result has been showed by N. Adli et. al., the particle grains of Sn0.7Cu with 1 wt% Al are formed in almost same size and shape. Li Yang et. al. explained that microstructure refinement was caused by dissolution of Al atoms into β-Sn and eutectic [31]. The solid solution strengthening by Al modified the microstructure of the intermetallic to becomes finer and more uniform, which results in a better strength of solder joint [32, 33]. This is due to the fact that smaller grain size will give a larger surface of grain boundaries. Plevachuk et. al. [34] stated that, Cu-Al phase is considered softer than Cu₆Sn₅, which may increase the ductility characteristic to solder alloy. Nevertheless, some black particles are also can be seen in Fig 4 (b-e). These particles are isolated Al and agglomerated Cu.

Fig 4: The microstructure of Sn-0.7Cu-xAl (0.01 – 0.075 wt%) under optical microscope. (a) 0wt% Al, (b) 0.01wt% Al, (c) 0.025wt% Al, (d) 0.05wt% Al, and (e) 0.075wt% Al [31].
In summary, the microstructure of solder alloy with Al addition was systematically reviewed in this paper.

- It would seem that the microstructure of lead-free solder alloy was significantly refined with a proper amount of Al addition. The mechanical properties will be enhanced by the finer microstructure as it can impede dislocation motion of atoms.

- However, excessive Al addition will cause the formation of Al-rich phases. The Al-rich particles have high potential to act as a heterogeneous nucleation site, which will reduce the degree of undercooling.

- Lastly, the formations of Cu-Al and Ag-Al IMCs have suppressed the formation of Cu₆Sn₅ and Ag₃Sn IMCs. As a result, the interdendritic region is getting lesser.

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