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Effect of Al addition on the bulk alloy microstructure properties of Sn-1Ag-0.5Cu solder

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Abstract: This study investigated the effect of the addition of 0.2, 0.5 and 1 wt% Al on the bulk alloy microstructural formation of Sn-1Ag-0.5Cu (SAC105). The typical bulk alloy microstructure of SAC105 is composed of large primary Sn grains and a mixture of Ag_3Sn and Cu_6Sn_5 intermetallic compounds (IMCs) which are in the form discontinuous particles at grain boundaries. It is found that the addition of Al to SAC105 alloy gradually suppresses the formation of the bulk Ag_3Sn and Cu_6Sn_5 IMC particles. The addition of 0.2% Al reduces the number of Ag_3Sn and replaces the Cu_6Sn_5, and forms Al-Ag and Al-Cu IMC particles, while the addition of 0.5% Al suppresses the formation of both Ag_3Sn and Cu_6Sn_5 IMC particles. The addition of 1% Al suppresses the formation of both Ag_3Sn and Cu_6Sn_5, and produces Al-Ag, Al-Cu and Al-rich IMC particles. It is also found that increasing the Al content from 0.2% to 1% refines the primary Sn-grains and significantly affects the size and final morphology of the IMCs developed in the bulk alloy. The observation above suggests that the addition of Al makes a big difference in the bulk alloy microstructure of SAC105 alloy. Therefore, one must expect much difference in bulk alloy mechanical properties. This paper is new in the aspect of effect of minor-alloy addition on the bulk alloy microstructure properties of Sn-1Ag-0.5Cu lead-free solder alloy

Keywords: SAC105 alloy, Al addition, bulk alloy microstructure, IMCs formation, Sn-rich grains.

Vpliv dodatka Al na mikrostrukturne lastnosti zlitine Sn-1Ag-0.5Cu

Izvleček: Delo raziskuje vpliv dodatka Al v višini 0.2, 0.5 in 1 wt% Al on na mikrostrukturo zlitine Sn-1Ag-0.5Cu (SAC105). Tipična mikrostruktura zlitine SAC105 sestoji iz velikih primarnih Sn zrn in mešanico Ag_3Sn in Cu_6Sn_5 intermetalnih sestavin (IMCs), ki se nahajajo v obliki diskontinuirnih delcih na robovih zrn. Ugotovljeno je bilo, da dodatek Al postopno zmanjšuje formacijo Ag_3Sn in Cu_6Sn_5 IMC delcev. Dodatek 0.2 % Al zmanjša število Ag_3Sn in jih zamenja z Cu_6Sn_5 pri čemer se formirajo Al-Ag in Al-Cu IMC delci. Pri dodatku 0.5% Al se zmanjša pojav tako Ag_3Sn kakor tudi Cu_6Sn_5 IMC delcev. Dodatek 1% Al zmanša formacijo Ag_3Sn in Cu_6Sn_5 ter sproži pojav Al-Ag, Al-Cu in Al bogatih IMC delcev. Poleg tega dodajanjeod 0.2 % do 1 % Al čisti primarna Sn zrna in močno vpliva na končno morfologijo IMC-ja v zlitini. Opazovanja predlagajo, da ima dodajanje Al velik vpliv na mikrostrukturo zlitine SAC105, kar vodi v različne mehanične lastnosti zlitine. Članek predstavlja nov pogled na vpliv manjšinske zlitine na mehanične lastnosti primarne zlitine pri brezsvinčeni spajki Sn-1Ag-0.5Cu.

Ključne besede: zlitina SAC105, dodatek Al, mikrostruktura zlitine, formacija IMCja, zrna bogata s Sn.

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1. Introduction

Traditionally, tin-lead solder alloy has been the main soldering material for a long time for its superior performance and low cost in modern electronic packaging. The presence of lead in tin-based solder alloys, mostly in the composition of eutectic 63Sn-37Pb, makes the solder superior in terms of thermal and mechanical characteristics for microelectronic assembly and reliability. However, the inherent toxicity of lead has raised serious environmental and public health concerns (Abtew and Selvaduray 2000; Amagai, Watanabe et al. 2002). The near eutectic Sn-Ag-Cu, e.g., SAC305 and SAC405 solder alloys have been considered as promising replacements for the lead-containing solders of microelectronics applications. However, due to the rigidity of the near eutectic SAC alloys, compared with the Pb-containing alloys, more failures have been found in the drop and high impact applications for portable electronic products (Chong, Che et al. 2006; Huang, Hwang et al. 2007). Moreover, the price competitiveness of near eutectic SAC is a weak point due to the high price of Ag (Yu, Jang et al. 2010). Hence, there is a demand for a more inexpensive and more reliable lead-free solder as a replacement for the near eutectic SAC alloys. Low Ag SAC (e.g., SAC105) was considered a solution for resolving both issues (Kittidacha, Kanjanavikat et al. 2008). However, this approach compromised thermal cycling performance, thus limiting their potential applications in the electronic industries (Huang, Hwang et al. 2007; Kittidacha, Kanjanavikat et al. 2008; Yu, Jang et al. 2010). To help improve the thermal cycling performance of the low Ag SAC, some minor-alloying elements were added to improve fatigue resistivity in bulk solder and strengthen the IMC layer (Huang, Hwang et al. 2007; Kittidacha, Kanjanavikat et al. 2008; Yu, Jang et al. 2010). However, there is a paucity of research on these alloys. The performance issues with near eutectic SAC alloys have forced solder ball suppliers to propose the modified alloys with the low Ag content, and with minor-alloy additions (Henshall, Healey et al. 2008; Kittidacha, Kanjanavikat et al. 2008; Henshall, Healey et al. 2009). The net result of minor-alloying addition is to either (1) alter the bulk alloy characteristics by changing the bulk microstructure and altering the formation and growth of the IMC particles in the bulk solder itself, or (2) control the interfacial IMC layer(s). Pandher et al. (2007) recently published findings that suggest the addition of bismuth (Bi) to SAC0307 alloys contributes to a refinement of grain structure of the bulk solder which improves the thermal cycling performance. Liu et al. (2009) reported that the addition of Mn or Ce to SAC105 solder alloys contributes to the formation of fine and stable IMC particles in the bulk solder which in turn improves the thermal cycling performance. Terashima and et al. (2004) found that the addition of Ni to Sn-1.2Ag-0.5Cu solder alloys contributes a network structure forming around the primary Sn grains in the initial microstructure of the bulk solder, resulting in good thermal fatigue resistance. Given these findings, it is necessary to investigate the influence of further addition of minor alloying elements on the micro-structural formation of the low Ag content SAC lead-free solders. In this paper, the Sn-1Ag-0.5Cu was selected as the basic solder system for exploring the micro-structural formation. The Al was selected as a minor addition, here the influence of the addition of different amount of Al element, 0.2, 0.5 and 1 wt%, on the micro-structural formation of Sn-1Ag-0.5Cu solder was systematically investigated and much attention was paid to the final morphology of bulk intermetallic compounds distributing in the solidified structures.

2. Experimental procedures

The Sn-1Ag-0.5Cu, Sn-1Ag-0.5Cu-0.2Al, Sn-1Ag-0.5Cu-0.5Al and Sn-1.0Ag-0.5Cu-1Al bulk solder specimens

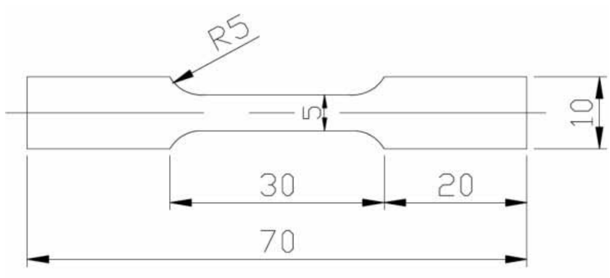

Figure 1: Solder bar specimen

with flat dog-bone shapes were used in this study. Figure 1 shows the solder bar specimen and its dimensions. The thickness of the solder bar is 5 mm. The dog-bone specimens were prepared by melting the Al with pure Tin ingot using an induction melting furnace to make the master alloy (Sn+2wt% Al). Following that, the master alloy was sent to a third party lab (SGS) for composition analysis to confirm the Al concentration. The Sn-Al, Sn-Ag and Sn-Cu master alloy with pure Tin was then melted in the heating furnace in an atmosphere environment. The solder was maintained at 300ºC temperature, after which the liquid solder was mixed for 30 minutes by the mixer to prevent the element from separating. After checking to ensure that the Sn, Ag, Cu and impurity of the alloy composition met the specification set by the Atomic Emission Spectrometry (AES), the solder ingots were cast in aluminum molds and naturally-air cooled from 300ºC to room temperature (25ºC). Then, the solder ingots were re-melted and cast in aluminum dog-bone molds, which had been preheated and kept at a temperature close to the solder alloy melting point. Finally, the molds were cold to the room temperature, disassembled the dog-bone samples were removed and visually inspected to ensure that the surface of the parallel area was without damage and voids. The microstructures of the solders were analyzed based on the Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy analysis (EDS) and scanning elemental maps. The SEM specimens were prepared by the dicing, resin molding, grinding and polishing processes. They were ground with four grades of SiC paper (# 800, #1200, #2400 and #4000), and then mechanically polished with a diamond suspension (3µm). Finally, the specimens were polished with colloidal silica suspension (0.04µm).

3. Results and discussion

A comparison of the equilibrium microstructures of the solidified lead-free solders would be very useful to clarify how the addition of Al element affects the solidified morphology. Figure 2 presents a SEM micro-structural picture of Sn-1Ag-0.5Cu, Sn-1Ag-0.5Cu-0.2Al, Sn-1Ag-

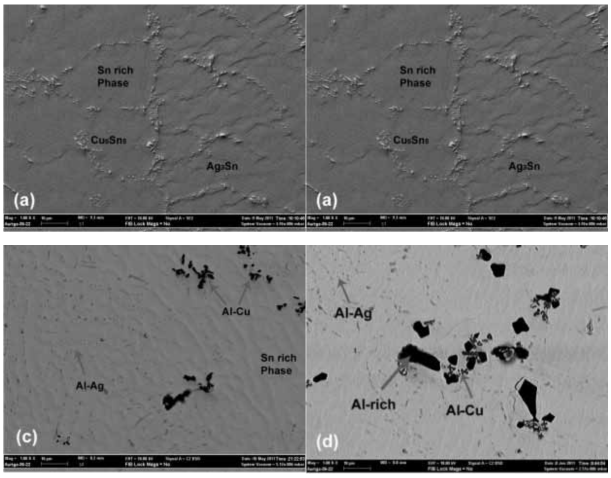

Figure 2: SEM micrograph of (a) Sn-1Ag-0.5Cu, (b) Sn-1Ag-0.5Cu-0.2A, (c) Sn-1Ag-0.5Cu-0.5A (1000X)

0.5Cu-0.5Al and Sn-1Ag-0.5Cu-1Al respectively. It is obvious that the microstructures of the Sn-1Ag-0.5Cu-*x*Al alloys are significantly different from the microstructure of Sn-1Ag-0.5Cu alloy.

The bulk alloy microstructure of Sn-1Ag-0.5Cu, as shown in Figure 2a, is composed of large primary Sn grains and two types of IMC particles which are in the form discontinuous particles at grain boundaries. These IMC particles are Ag14.40 in wt%-Sn85.60 and Cu24.95-Sn71.33-Ag03.72, as indicated in the EDS analysis results (see Figure 3), which are speculated to be Ag_3Sn and Cu_6Sn_5 IMC particles, respectively. The Ag_3Sn and Cu_6Sn_5 IMC particles possess much higher strength than the bulk material in SAC solder, whereas primary Sn has the lowest elastic modulus and lowest yield strength among the constituent phases in SAC solder (Kim, Suh et al. 2007; Suh, Kim et al. 2007). It is well known that the mechanical properties of an alloy consisting of a ductile phase and a hard brittle phase will depend on how the brittle phase is distributed in the microstructure. If the brittle phase is present as grain boundary envelope, the alloy is brittle. If the brittle phase is in the form discontinuous particles at grain boundaries, the brittleness of the alloy is reduced (Dieter 1961). In light of the above mechanism, the SAC105 bulk solder is expected to exhibit high elastic compliance (i.e., low elastic modulus) and high plasticity (i.e., low yield strength) which are identified as key for higher drop resistance.

The bulk alloy microstructure of Sn-1Ag-0.5Cu-0.2Al, as shown in Figure 2b, is composed of large primary Sn grains and three types of IMC particles. The gray large particle is Al6.55-Ag76.34-Sn17.12, and the dark large particle is Al30.47-Cu58.82-Ag3.19-Sn7.52, as indicated in the EDS analysis results (see Figure 4a and 4b). Presumably those particles are primarily IMC of Al-Ag and Al-Cu partially mixed with Sn. The bright fine particles shown in Figure 2b are Sn53.98-Ag46.02, as indicated in the EDS analysis results (see Figures 4c).The bright fine particles are speculated to be Ag_3Sn IMC particles. Figure 5 shows scanning elemental maps of the Sn-1Ag-0.5Cu-0.2Al solder. It is found that the concentration of Ag, Cu and Al has a sudden rise at the location

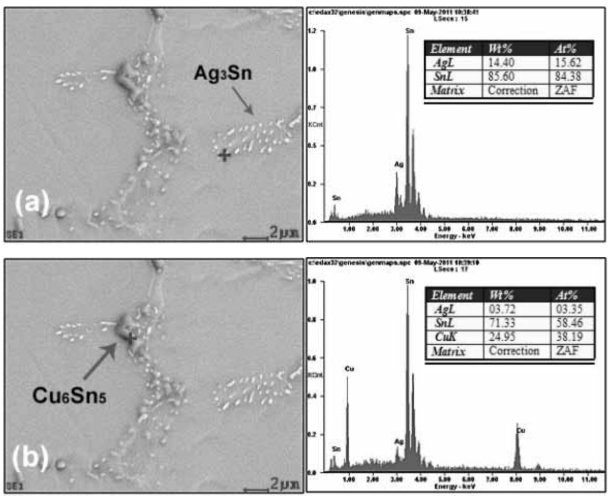

Figure 3: EDS analysis result of the bulk IMC particles in the Sn-1Ag-0.5Cu

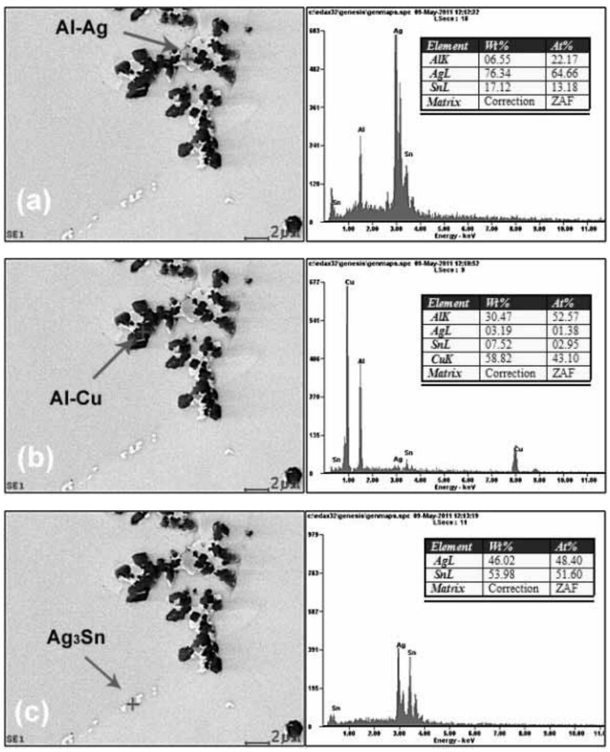

Figure 4: EDS analysis result of the bulk IMC particles in the Sn-1Ag-0.5Cu-0.2Al of (a) Al-Ag, (b) Al-Cu, (c) Ag_3Sn

Figure 5: Scanning elemental maps of the Sn-1Ag-0.5Cu-0.2Al

of the bulk IMC particles. The concentration of Sn becomes small at the location of the bulk IMC particles. All these indicate that elements Ag, Cu and Al constitute the bulk IMC particles with minor Sn dissolving. It can be seen from Figures 2b and 5 that the Al-Ag and Al-Cu are sparsely distributed at and nearby the grain boundaries, beside the Ag_3Sn particle.

The addition of 0.2% Al into SAC105 bulk alloy reduces the number of Ag_3Sn and replaces the Cu_6Sn_5 IMC particles, and forms large Al-Ag and Al-Cu IMC particles. Namely, the Ag and Cu in this alloy will be drained from the solder matrix to react with Al to form large Al-Ag and Al-Cu IMC particles. This is at least in correspondence with the anticipation that Al has solubility in Ag and Cu (Hanson 1985), and very limiting solubility in Sn (Hanson 1985). It is well known that fine particles in alloys impede dislocation movement more efficiently, and produce an alloy with greater yield strength. When these particles grow in size, the yield strength decreases. In addition, when the coherency of particles within the matrix is gradually lost with particles growing, the yield strength is further decreased (Dieter 1976). In light of the above mechanism, beside the discontinuous form of the IMC particles at the grain boundaries (see Figure 6), the 0.2% Al-containing bulk solder is

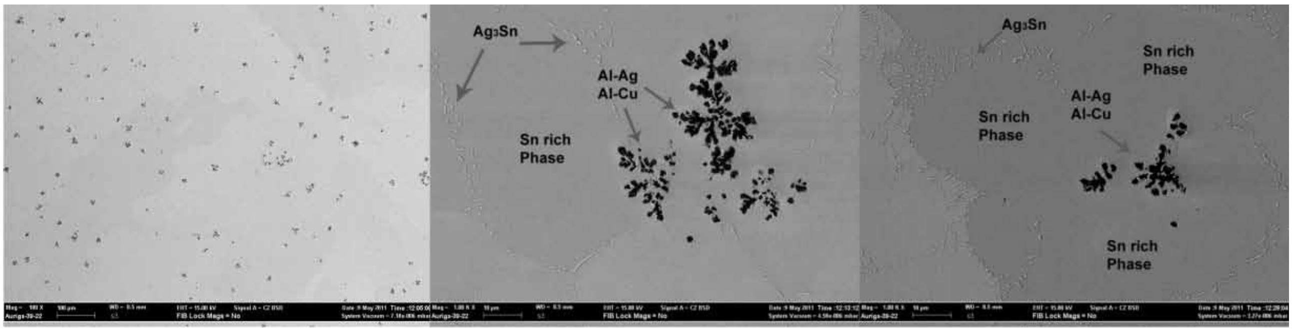

Figure 6: SEM micrograph of Sn-1Ag-0.5Cu-0.2A (100X-1000X)

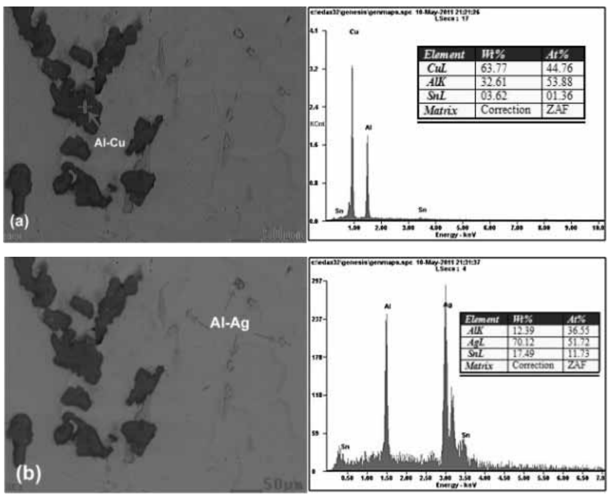

Figure 7: EDS analysis result of the bulk IMC particles in the Sn-1Ag-0.5Cu-0.5Al

expected to show low elastic modulus and low yield strength. The sparse distribution of Al-Ag and Al-Cu IMC particles within the matrix may help to reduce the unfilled interfaces of primary Sn grains at grain boundaries. It is well known that the strength of the interface between primary Sn grains to be lower than that of the primary Sn grains interface filled with the IMC particles.

The addition of 0.5% Al into SAC105 bulk alloy refines the Sn-rich grain structure and produces two types of IMC particles, as shown in Figure 2c. The gray fine particles are Al-Ag IMC particles and the large dark particles are Al-Cu IMC particles, as indicated in the EDS analysis results (see Figure 7) and elemental analysis (see Figure 8). It can be seen from Figure 9 that the large Al-Cu particles appeared sparsely within the Sn matrix. On the other hand, the fine Al-Ag IMC particles form network structure around the primary Sn grains.

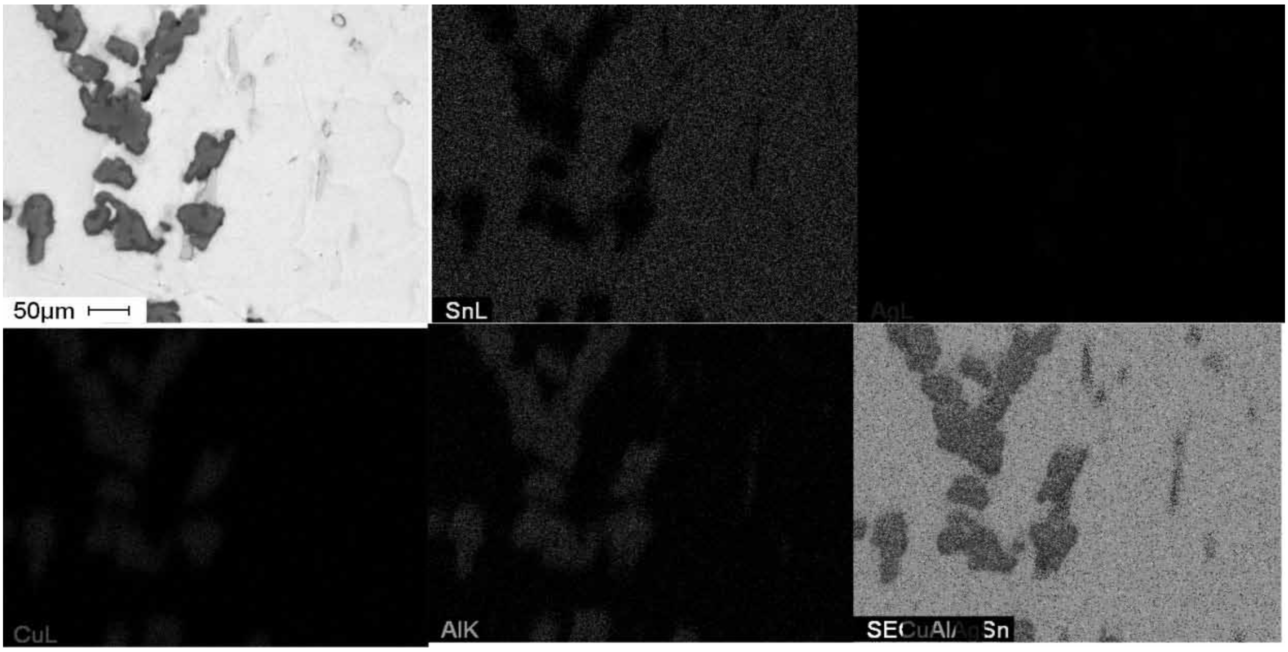

Figure 8: Scanning elemental maps of the Sn-1Ag-0.5Cu-0.5Al

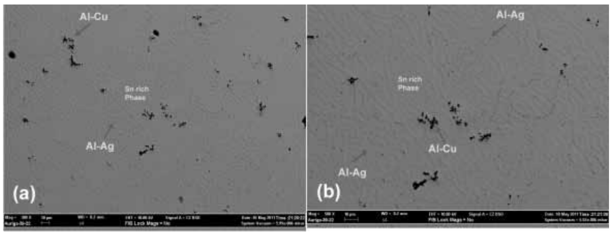

Figure 9: SEM micrograph of Sn-1Ag-0.5Cu-0.5A (a) 300X (b) 500X

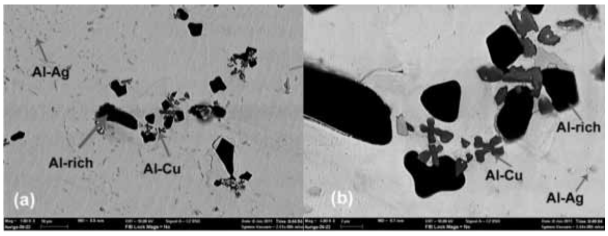

Figure 10: SEM micrograph of Sn-1Ag-0.5Cu-1Al: (a) 1000X, (b) 4000X

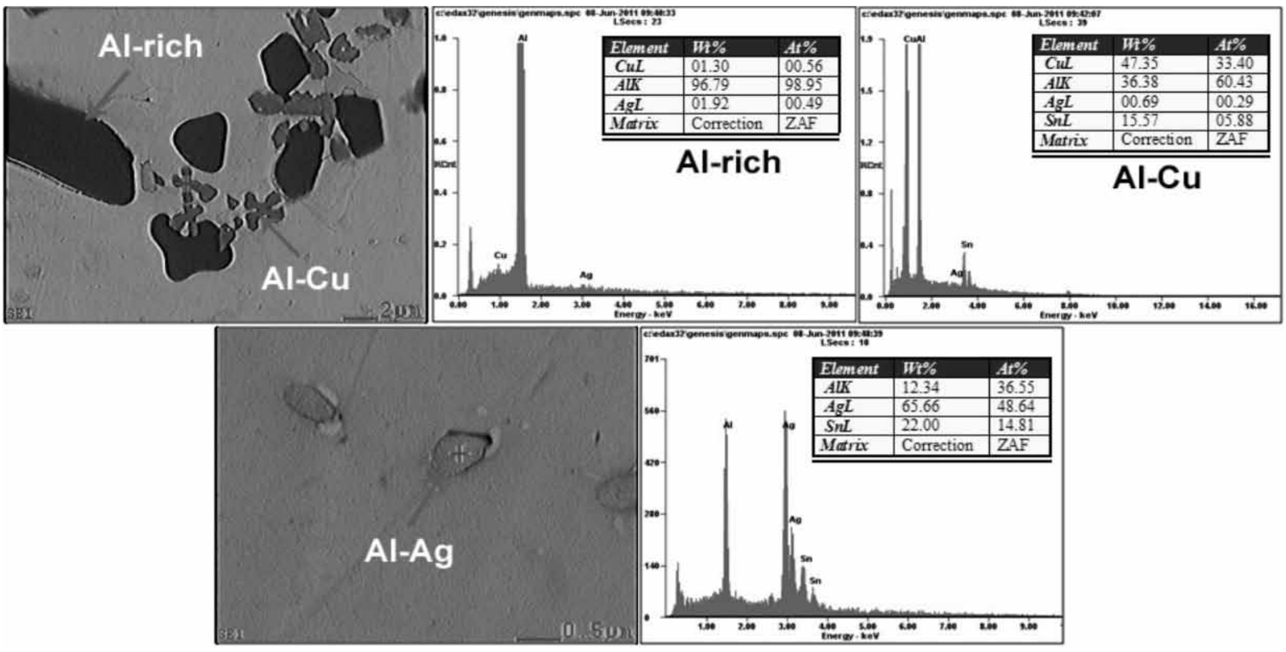

Figure 11: EDS analysis result of the bulk IMC particles in the Sn-1Ag-0.5Cu-1Al

The addition of 0.5% Al into SAC105 bulk solder suppresses the formation of the Ag_3Sn and Cu_6Sn_5 IMC particles, and forms fine Al-Ag IMC particles and large Al-Cu IMC particles. The fine Al-Ag IMC particles form network structure around the primary Sn grains which lead to refine the primary Sn grains of the bulk solder. It is well known that the presence of fine particles dispersed within the matrix can significantly suppress the dislocation movement. Hence, the presence of the fine Al-Ag IMC particles in the bulk alloy significantly strengthens the bulk solder. Therefore, the 0.5% Al-containing bulk solder is expected to show high yield strength and high elastic modulus.

The bulk alloy microstructure of Sn-1Ag-0.5Cu-1Al, as shown in Figure10, is composed of small primary Sn grains and three types of IMC particles. The Al-rich particles (dark large particles) are Al96.79-Ag1.92-Cu1.3, as indicated in EDS analysis results (see Figure 11). The gray large particles are Al36.38-Cu47.35-Ag0.69-Sn15.57, as indicated in the EDS analysis results (see Figure 11). The very fine gray particles are Al12.34-Ag65.66-Sn22, as indicated in the EDS analysis results (see Figure 11), which are speculated to be Al-Cu and Al-Ag IMC partially mixed with Sn, respectively. Figure 12 show that the bulk Al-rich and Al-Cu IMC particles are sparsely distributed within the matrix, whereas the fine Al-Ag IMC particles forms network structure around the primary Sn grains which leads to refine the primary Sn grains. Hence, the 0.5% Al addition is also expected to strengthen the bulk alloy.

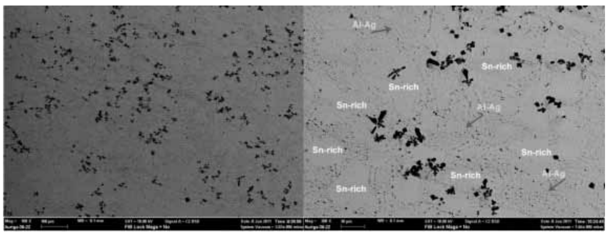

Figure 12: SEM micrograph of Sn-1Ag-0.5Cu-1Al

4. Conclusions

The effect of different Al addition (0.2 wt, 0.5 and 1 wt%) on the bulk alloy microstructure properties of the Sn-1Ag-0.5Cu alloy was investigated in this study. The conclusions can be summarized as follows:

The addition of Al to SAC105 bulk alloy gradually suppresses the formation of the Ag_3Sn and Cu_6Sn_5 IMC particles. The addition of 0.2% Al reduces the number of Ag_3Sn and suppresses the formation of the Cu_6Sn_5, and forms Al-Ag and Al-Cu IMC particles, while the addition of 0.5% Al suppresses the formation of both Ag_3Sn and Cu_6Sn_5 IMC particles. The addition of 1% Al suppresses the formation of both Ag_3Sn and $Cu_6Sn_{5,}$ and produces Al-Ag, Al-Cu and Al-rich IMC particles.

Increasing the Al content from 0.2% to 1% refines the primary Sn-grains and significantly affects the size and final morphology of the IMCs developed in the bulk alloy. The addition of 0.2wt% Al produces large Al-Ag and Al-Cu IMC particles, whereas the addition of 0.5wt% Al produces fine Al-Ag and large Al-Cu IMC particles. The addition of 1 wt% Al forms fine Al-Ag and large Al-rich and Al-Cu IMC particles. The fine particles form network structure around the primary Sn grains which leads to refine the primary Sn grains, while the large particles sparsely distributed within the matrix
The observation above suggests that the addition of Al makes a big difference in the bulk alloy microstructure of SAC105 alloy. Therefore, one must expect much difference in bulk alloy mechanical properties.

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