Microstructure Evolution of Sn-3Ag-3Bi-3In/Cu Lead-free Solder Joints during Interval Aging

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Abstract. The microstructure evolution of Sn-3Ag-3Bi-3In/Cu lead free solder joints was investigated over interval aging mode to simulate the real application environment. The solder joints were aged at 150 °C for 48h, 96h, 144h, 196h and 240h, respectively. Results demonstrate that the IMC layer of Sn-3Ag-3Bi-3In/Cu solder joints evolves from scallop shape to layer shape and becomes thicker simultaneously with increasing aging time. It is noteworthy that the IMC layer is composed of only Cu6(Sn, In)5 phase without Cu3(Sn, In) phase during interval aging for various aging time. As a result, the reliability of Sn-3Ag-3Bi-3In/Cu solder joints can be improved due to the lack of Cu3(Sn, in) phase which is detrimental to reliability over interval aging mode. Moreover, it is observed that diffusion control mechanism is fit for the growth of IMC layer of all solder joints over both interval and continuous aging mode. Further, the growth formula of IMC layer of Sn-3Ag-3Bi-3In/Cu solder joints is revealed as \( X = 2.56 + 0.062t^{1/2} \), in addition, the diffusion coefficient of is obtained as 0.02491 \( \mu \)m²/h.

1. Introduction

Nowadays, with the rapid economic development and the demand of satisfying human life, the pollution of environment and health is getting worse. As lead is inherent toxicity not only to environment but also to human beings’ nervous system, in particular, recycling lead in electronics should pay more cost and efforts than that in batteries or cathode ray tubes (CRT) due to the difficulty in removing it from the components [1, 2], most of countries have legislated strictly to ban the use of lead and lead-containing alloys.

Simultaneously, material scholars have been dedicating tremendous efforts on developing lead-free solders as a replacement of Sn-37Pb eutectic solder [3], mainly based on the four requirements: (1) low melting point, low melting point of lead-free solder joints can avoid thermal damage to electronic packages, it should be close to the melting point of Sn-37Pb eutectic alloy; (2) wettability, good wettability could provide reliable bonding between components and circuit pads; (3) property, good mechanical properties and electronic properties can improve the reliability of solder joints; (4) cost, the last but the most important one, low cost is better unless it has more outstanding performance. Under the guidance of these principles, scholars developed binary Sn-based alloys such as Sn-Zn, Sn-Bi, Sn-Cu alloy successively. As binary alloy is hard to meet the requirement of solder, ternary Sn-based alloys emerged due to scholars’ efforts, which are Sn-Zn-Bi, Sn-Ag-Zn, Sn-Ag-Cu alloy and etc.
Among these alloys, Sn-3.0Ag-0.5Cu (SAC305) alloy has attracted the most attention owing to its good wettability, thermal fatigue characteristics and mechanical properties.

As well known, Sn-37Pb eutectic solder shows excellent wettability and low melting point, that is the main reason why it is hard to be prohibited until legislation in most of countries. Although the wettability of Sn-3.0Ag-0.5Cu (SAC305) alloy is better than other ternary Sn-based lead-free alloys, it can’t compare with Sn-37Pb eutectic solder. Therefore, scholars keep on developing better alternative lead-free solders. Shalaby [4] investigated the effects of In and Ag additions on the structure, mechanical, creep properties, melting point of Bi-Sn lead-free solder alloys and compared with traditional Sn-Pb eutectic alloy, results stated the In and Ag containing solder alloy exhibited a good combination of higher creep resistance, good mechanical properties and lower melting temperature as compared with Pb-Sn eutectic solder alloy. El-Daly [5] analyzed Sn-Ag-Cu-Bi solders and compared with Sn-1.5Ag-0.7Cu (SAC157) alloy, they observed that the precipitation of these Bi atoms or particles could significantly refine the microstructure, blocked the movement of dislocations and increased the creep resistance of Bi-containing solders. Liu [6] identified the intermetallic compound with different morphologies and illustrated the characterization during solid-state aging at 60°C, the morphology of fine-grain Cu2(In,Sn) kept granule-type, while the coarse-grain Cu2(In,Sn) was substrate-dependent with elongated morphology. As mentioned above, Bi can refine microstructure, and improve creep resistance, moreover, In and Ag atoms can increase mechanical properties and lower melting point. Hence, Sn-3Ag-3Bi-3In solder alloy was investigated in the study.

Considering a number of electronic products don’t serve continuously during one day, there could be some differences from the growth behavior of IMCs over different aging modes. In order to investigate the growth of IMCs in the real application environment, we adopt the interval aging mode to simulate the real application environment. Thus, the aim of the paper is to research the growth character of Sn-3Ag-3Bi-3In/Cu solder joints during interval aging.

2. Experimental Procedures

The commercial copper plates with dimensions of 15 mm×15 mm×3 mm were used as the substrates in this study. The copper substrates were ground with silicon carbide paper and polished with 0.25μm diamond paste until a mirror surface was obtained. The prepared substrates were then dipped into 5% (by volume) nitric acid (HNO3) to remove oxide layer. Sn-3Ag-3Bi-3In solder paste was then placed on the substrates with a diameter of 5 mm as shown in Fig.1. Further, solder joints were formed with a F4N infrared reflow furnace. The specimens were reflowed at above liquidus temperature but the peak temperature wasn’t beyond 210°C for 250s. The typical reflow temperature profile for one cycle is shown in Fig. 1.

![Figure 1. Typical reflowing temperature profile for one cycle of the solder joints.](image)

After reflowing, the prepared solder joints were performed isothermal aging experiment in an vacuum drying oven at 150°C for 48h, 96h 144h, 192h and 240h, respectively. Most importantly, the interval aging was adopted in our study, namely, the solder joints were aged continuously for 17 hours and then stopped aging for 7 hours, at this stage, it is worthy noted that the effective aging time which
we calculated is the continuous 17 hours. The operation was repeated until the total time reached 48h, 96h, 144h, 192h, and 240h, respectively.

In order to investigate the formation and evolution of interfacial IMCs, specimens were sectioned perpendicularly to the solder/copper interface of the solder joints and mounted in Klarmount. They were successively ground down to 400, 800, and 1000 grit using silicon carbide paper cooled with flowing water, and polished with 5μm Al2O3 suspension followed by 0.25μm diamond paste. The interfacial morphologies of solder joints were observed by a Scanning Electron Microscope (SEM, ZEISS-EVO18) equipped with an Energy Dispersive X-ray Spectrometer (EDS).

Considering the reliable and repeatable data of the mean thickness of IMCs layer, three solder joint samples for each aging time were used, SEM image analysis software was then employed to digitally measure the areas of each sample’s IMCs layers from left side to right side. The thickness of IMCs layers is determined by the area of the IMCs layer dividing its length, and the mean thickness of IMCs layers was then calculated by averaging the data.

3. Results and Discussion

The backscattered electron microscope images in Fig. 2(a-e) show the IMC layers formed in Sn-3Ag-3Bi-3In/Cu solder joints aged at 150°C for 48h, 96h, 144h, 192h and 240h, respectively. It can be seen that the IMC layer in Fig.2 (a) is dark gray with the morphology of scallop shape, which is Cu6(Sn, In)5 phase. A slice of big white part above the IMC layer is compound composed of Sn, Bi, In, and Cu atoms, and quite a few small dot in Sn matrix mainly is Ag3Sn, some needle part is probably Cu2(In,Sn). With aging time increasing, the IMC layer is become thicker, but they are still scallop shape. It is remarkable that the white compound on top of IMC layer grows uniformly on the IMC layer. As aged for 144h, each microstructure grows larger, the needle plates become lamellar structure and nearly connect with bulk white compound of BiInSnCu, consequently, the three phases from substrate to matrix is IMC layer, BiInSnCu compound and Cu2(In,Sn) compound consecutively as shown in Fig.2 (c). Unfortunately, Cu3(Sn, In) phase doesn’t appear in the IMC layer yet. With the aging time reached 192h, there are some differences from the former ones. The IMC layer becomes layer shape gradually and the bulk white compound evolves uneven on the IMC layer, meanwhile, lamellar structures also decrease and quite a few of them change to dot structure. From Fig.2 (e), the IMC layer is nearly layer shape as aged for 240h. In addition, the white bulk shape on IMC layer vanishes, instead, they move to the matrix and separate to several parts, moreover, all of the lamellar structures almost evolve to dot structure. However, the IMC layer is still monolayer, there is no Cu3(Sn, In) phase at all.

As Cu3(Sn, In) phase doesn’t appear in this study, considering reflow temperature and time, aging temperature and mode, it is mainly the interval aging mode which contribute to only Cu6(Sn, In)5 phase existed in IMC layer. According to transformation kinetics, Cu6(Sn, In)5 phase is unstable, it can transmit to stable Cu3(Sn, In) phase as the free energy is large enough under available condition. During interval aging, the accumulation of free energy isn’t continuous yet, and it is hard to accumulate large enough to overcome kinetic energy obstacle, hence, in this study, Cu6(Sn, In)5 phase doesn’t transmit to Cu3(Sn, In) phase, thus it leads to only one layer in IMC layer in Fig.2.

Considering the reliability of solder joint, Cu3(Sn, In) phase is detrimental to the reliability of Sn-3Ag-3Bi-3In/Cu solder joints, so the result that the lack of Cu3(Sn, In) phase in IMC layer in our study is benefit to reliability.

From the reliability of solder joints, it isn’t expected that the IMC layer grows thickly, as a result, the thickness of IMC layer is one of the criteria. According to the classical diffusion mechanism, generally the growth of the interfacial IMC layer is controlled by bulk diffusion when the growth exponent is equal to 1/2, where the interfacial reaction occurs at the interface between the solid solder and solid substrate.

Due to the interval aging mode in this study, it is uncertain that the growth of IMC layer follows classical diffusion mechanism. Therefore, the thickness of IMC layer is measured and plotted with aging time to identify the growth mechanism. Fig.3 shows the thickness of the interfacial IMC layers
as a function of square root of the aging time. It is clearly seen that the thickness of IMC layer increases linearly with the aging time, indicating that the growth of IMCs layer after aging follows diffusion control mechanism. Consequently, it is observed that the growth of Sn-3Ag-3Bi-3In/Cu solder joints during interval aging follows diffusion control mechanism. Furthermore, it is inferred that the diffusion control mechanism also can be used for interval aging mode, which is in accordance with our previous results [7].

Figure 2. Interfacial SEM images of IMC layer during aging at 150°C for (a) 48h, (b) 96h, (c) 144h, (d) 196h and (e) 240h.

Considering that the IMC growth during continuous aging is also diffusion control mechanism [8, 9], as a result, it is observed that diffusion control mechanism is fit for the growth of IMC layer of all solder joints over both interval and continuous aging mode.
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Figure 3. Interfacial IMC thickness of Sn-3Ag-3Bi-3In/Cu joints with different aging time.

By linear regression, the thickness of IMC layer follows square root of time power law relationship that can be expressed as $X=2.56+0.062t^{1/2}$, the slope of the curve shown in Fig. 3 gives the $k$ value, which is 0.062 in this study. In particular, $k$ is also the growth rate constant, as it is diffusion controlled mechanism, $k$ is a function of diffusion coefficient, which is $k=D^{1/2}$. Therefore, it can be easily calculated the diffusion coefficient of Sn-3Ag-3Bi-3In/Cu solder joints, which is 0.02491 $\mu$m$^2$/h.

4. Conclusion
Experimental studies were carried out for various aging times on Sn-3Ag-3Bi-3In/Cu lead-free solder joints during interval aging. The following conclusions can be drawn from the present research:

1) IMC layer of Sn-3Ag-3Bi-3In/Cu solder joints evolves from scallop shape to near layer shape accompanied with thicker with increasing aging time, meanwhile, the compound of BiInSnCu undergoes several structures during interval aging.

2) The IMC layer is composed of only Cu$_6$(Sn, In) phase without of Cu$_3$(Sn, In) phase for various aging time. Nevertheless, the reliability of Sn-3Ag-3Bi-3In/Cu lead-free solder joints can be improved due to the lack of Cu$_3$(Sn, In) phase, which is detrimental to the reliability of solder joints.

3) The growth of IMC layer of Sn-3Ag-3Bi-3In/Cu solder joints follows diffusion control mode. Most importantly, it is revealed that the diffusion control mode is fit for IMC layer growth of all solder joints over interval aging mode.

4) The growth equation of Sn-3Ag-3Bi-3In/Cu solder joints is observed as $X=2.56+0.062t^{1/2}$, further, the diffusion coefficient $D$ is revealed as 0.02491 $\mu$m$^2$/h.

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