Interfacial intermetallic developments of Sn-3.0Ag-0.5Cu-2.0ZnO lead free solder

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Abstract: The interfacial intermetallic compound growth behavior of Sn-3.0Ag-0.5Cu lead free solder joints with 2.0wt.% ZnO of micrometer was investigated in this study. Solder joints were fabricated in F4N reflow furnace at 255℃for less than 5min and thereafter aged at 150℃up to 240h. Results showed that the IMCs layer were almost layer type and grew thicker with extended aging time. The IMCs of Sn-3.0Ag-0.5Cu-2.0ZnO composite solder was diffusion controlled mechanism by diffusion growth kinetics analysis, moreover, the diffusion coefficient of Sn-3.0Ag-0.5Cu-2.0ZnO composite solder was 0.31 μm²/h and smaller than that of Sn-3.0Ag-0.5Cu plain solder, it revealed that ZnO powder can reduced the diffusion coefficient of interfacial intermetallic compound.

1. Introduction

Lead free solder has been recently replaced Sn-Pb alloy and widely applied in electronic packaging fields owing to the toxicity of Sn-Pb solder, for it is not only harmful to environment which has attracted individuals’ growing attention, but also detrimental to folks’ nervous system or even damaged children’s intelligence quotient[1]. Hence most of countries have legislated to forbid the use of Pb. Under this circumstance, scholars have dedicated to exploring several different solder systems, for example, Sn-Zn-Ag alloy, Sn-Bi-Zn alloy, Sn-Ag-Cu alloy, etc. Among these alloys, Sn-Ag-Cu system is considered to be the most promising solder. Similarly, Sn-3.8Ag-0.7Cu alloy are widely applied in European Union, Sn-3.9Ag-0.6Cu is famous in US, whereas Sn-3.0Ag-0.5Cu is mainly in Japan and other Sn-1.0Ag-0.7Cu alloy[2]. According to wettability, melting characteristic, mechanical properties of solders, Sn-3.0Ag-0.5Cu alloy is considered better up to now.

Reliability of solder joints is extremely fundamental to the performance and service time of electronic components. Usually, the reliability can be assessed from wettability, melting characteristic, mechanical properties and so on, as the properties can be generally reflected from microstructure, as well as the interfacial morphology is crucial to solder joint, therefore, the interfacial morphology of solder joint can estimate the reliability of solder joints. To a solder joint, an intermetallic compound (IMC) layer can form and grow between copper substrate and solder which is interface during soldering and aging. A proper thickness of IMC layer is benefit to the reliability of solder joint, nevertheless, a much thinner IMC layer may lead to a weak combination or a thicker layer can form brittle phase which declines the mechanical properties and finally both reduce the reliability of solder joints. Actually, with the service time extended, the IMC layer would be too thick to service. Accordingly, a better way to improve the reliability of solder joints is to control the thickness of IMC layer.

With the development of miniaturization of electronic products, a better reliability of solder joint is needed to meet the increasing requirement. Consequently, researchers has explored multicomponent
alloy with trace element such as Ni, RE, Bi, Co and other elements, Li et al. [3] investigated the shear strength and interfacial microstructure of Sn-9Zn/Ni joints with Co, they revealed that Co was not only a diffusion barrier as well as react element and refined the interfacial microstructure. Tu et al. [4] researched the influence of Ce on the thermal behavior, microstructure, and mechanical properties of Sn-3.0Ag-0.5Cu (SAC305) solder alloy, it showed that thinner IMC layers and slower IMC growth rate can be obtained with addition of Ce. Despite trace alloy element can refine the microstructure, it can form brittle phase which is unexpected. Thereby, scholars has modified the solder with foreign reinforcement which would not react with solder and copper substrate, Li et al. [5] studied the addition of TiO2 on micro-scale Sn-3.0Ag-0.5Cu solder with different joint size, results showed that both the thickness and grain size of the intermetallic compound (IMC) increased with the increase in joint size. Hu et al. [6] studied Sn3.0Ag0.5Cu solder with Cu6Sn5 intermetallic particles, they manifested that nanoparticles addition could effectively suppressed the growth of interfacial IMCs layers. Although the above report implies that nanoparticle addition can refine the microstructure, but there are scarce report about the performance of micro-ZnO particles on Sn3.0Ag0.5Cu solder. Hence, the aim of this study is to explore the growth behavior of Sn3.0Ag0.5Cu solder with 2.0wt.% particles.

2. Experimental Procedure
ZnO particles with 30 μm size, Sn-3.0Ag-0.5Cu powder with 25-40 μm size and flux were used to fabricate composite solder. Commercial copper plate with purity of 99.9% was cut to 10×10×2mm to act as substrate. The solder joints were formed in a F4N reflow furnace for less than 5min with the maximum temperature of 255℃, subsequently the solder joints were aged in an vacuum drying oven for isothermal aging at 150 ℃ for 48h,96h,144h,192h and 240 h. After that, the solder joints were cut, ground and polished until the interface look like a mirror, then the corrosion agent was applied to corrode the specimen. 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).

SEM image analysis software was then employed to measure the areas of IMCs layers. The thickness of IMCs layer is determined by the area of the IMCs layer dividing its length, and the mean thickness was then calculated by averaging the data, in order to get the accurate data, ten solder joints samples were used to obtain a data.

3. Results and discussion
The interfacial morphologies of IMC layer aged at 150 ℃ for 48h,96h,144h,192h and 240 h are shown in Fig.1. It can be seen that a gray layer corresponded to IMC layer is between black part which is copper substrate and light gray part which is solder. Moreover, it is displayed that the IMC layer is composed of two parts, namely a dark gray layer of Cu₃Sn phase and a gray part of Cu₆Sn₅ phase. Interestingly, the IMC layer is flatter other than scallop type of Sn-3.0Ag-0.5Cu solder as reported by Hu[7]. This phenomenon maybe attributed to the effect of micro-ZnO particles. In addition, with aging time extended, both of Cu₆Sn₅ layer and Cu₃Sn layer are layer type as well as grow thicker as listed in Fig.1 from (a) to (e).
Fig. 1 SEM micrographs of interfacial IMC layer aged for various time: (a) 48h, (b) 96h, (c) 144h, (d) 192h, (e) 240h.

It is manifested that the IMC layer of Sn-3.0Ag-0.5Cu grows thicker and they follow diffusion control mode at aging stage, as well as the thickness of IMC layer is related to square root of aging time. However, the growth mode of Sn-3.0Ag-0.5Cu solder with 2.0wt%ZnO micrometer is still not clearly, we should make sure the growth mode of composite solder. Therefore, the thickness of IMC layer at various aging time are plotted with square root of aging time in Fig. 2. It is manifested that both of Sn-3.0Ag-0.5Cu solder and Sn-3.0Ag-0.5Cu-2.0ZnO composite solder grow with the same trend, it is worthy note that the IMCs thickness of Sn-3.0Ag-0.5Cu-2.0ZnO composite solder is linearly with square root of aging time, which is

\[ X = X_0 + K t^{1/2} \]  

(1)

where \( X \) is the IMCs thickness, \( t \) is aging time, \( K \) is coefficient which is related to diffusion coefficient, proceeding as

\[ K = D^{1/2} \]  

(2)
where $D$ is the diffusion coefficient. Consequently, it can be concluded that the growth of IMCs layer is diffusion controlled mechanism. Moreover, the growth equation of Sn-3.0Ag-0.5Cu solder and composite solder is as follows

$$X = 1.92 + 0.61t^{1/2} \quad (3)$$
$$X = 1.10 + 0.56t^{1/2} \quad (4)$$

From Eq.(2), the diffusion coefficient $D$ of Sn-3.0Ag-0.5Cu solder and Sn-3.0Ag-0.5Cu-2.0ZnO composite solder can be calculated, and they are 0.37 $\mu$m$^2$/h and 0.31 $\mu$m$^2$/h, respectively. Therefore, it is revealed that the IMCs growth of Sn-3.0Ag-0.5Cu-2.0ZnO composite solder is slower than that of plain solder. As they are both diffusion controlled growth, the smaller diffusion coefficient infers the atoms diffuse more slowly so as to lack atoms to form IMCs layer and lead to a thinner IMCs layer.

By comparing the thickness and diffusion coefficient of Sn-3.0Ag-0.5Cu-2.0ZnO composite solder and Sn-3.0Ag-0.5Cu plain solder, it can be obtained that the addition of 2.0 wt.% micro-ZnO particles can restrain the diffusion of atoms both from substrate and solder which finally form a thinner interfacial IMCs layer. Obviously, the reliability of solder joints can be improved due to a thinner IMCs layer, hence, the reliability of Sn-3.0Ag-0.5Cu solder joints can be promoted with the addition of 2.0 wt.% ZnO microparticles.

![Fig.2 Interfacial IMC thickness of solder joints with different aging time.](image)

**4. Conclusions**

The growth performance of Sn-3.0Ag-0.5Cu solder with 2.0 wt.% ZnO microparticles was investigated at isothermal aging for various aging time after reflowing, the following conclusions can be summarized:

(1) The interfacial IMCs layer of Sn-3.0Ag-0.5Cu-2.0ZnO composite solder is almost layer type with time extended.

(2) The IMCs layer of Sn-3.0Ag-0.5Cu-2.0ZnO composite solder is controlled by diffusion mechanism where the growth equation is $X = 1.10 + 0.56t^{1/2}$, moreover, the diffusion coefficient of solder is 0.31 $\mu$m$^2$/h which is smaller than that of Sn-3.0Ag-0.5Cu plain solder.

(3) The addition of 2.0 wt.% ZnO microparticles can inhibit the atoms diffusion both from substrate and solder thereby lead to a thinner IMCs layer.

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