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Growth behaviors of IMCs in low-silver lead-free Sn1.0Ag0.5Cu micro-joints for long-term high-temperature environments

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Abstract. Reliable, nontoxic and eco-friendly solders are gaining attention in welding. Low-silver lead-free solder becomes a developing trend. Herein, the microstructures of Low-silver lead-free Sn1.0Ag0.5Cu micro-joints at different storage time in high-temperature environments are observed and analysed in this article. It is our primary focus here to analyse the thickness evolution of the interfacial intermetallic compound (IMC) layer. The numerical growth models of IMC bilayers are constructed, which provide an essential reference for lifetime analysis and reliability evaluation of Sn1.0Ag0.5Cu solders for long-term use in high temperature environment.

1. Introduction

Due to lead toxicity, lead-free solders are used as substitutes for the traditional PbSn solders [1]. Tin-rich solder alloys, such as Sn-Cu [2], Sn-Ag [3] and Sn-Ag-Cu [4], have become popular alternatives to lead alloys. Of the various kinds of lead-free tin solders, Sn-Ag-Cu (SAC) solders have excellent comprehensive performance with good wettability and low melting points that they are well-recognized as the preferred alternative materials for tin-lead solders [5]. For example, high silver lead-free solders such as Sn3.0Ag0.5Cu alloys have been widely used in electronics due to their favorable strength and ductility. However, SAC solders still have some inadequacies. They exhibit high joint brittleness and relatively poor impact resistance with high Ag_3Sn content [6]. Additionally, they are costly [7]. For this reason, plenty of studies focused on low silver lead-free solders [8-10]. The low silver lead-free solders represented by Sn1.0Ag0.5Cu alloy are not inferior to PbSn solders in crucial welding characteristics, and are obviously superior to high silver lead-free solders in mechanical drop performance. Therefore, they are expected to replace lead tin solders in view of the overall performance. Whereas, the in-depth research and practice of low silver lead-free Sn1.0Ag0.5Cu solders are still in the primary exploration stage at present. Their high Sn content, high requirements on welding temperature and interface reaction may eventually pose a significant risk to reliability in lifetime service.

During service processes, both too "thick" and too "thin" thick IMC layers carry the potential for crack failures. Too thick IMC layers tends to degrade the toughness and shear strength. The fracture occurs at the interfaces instead of solder matrixes with IMC layers thickened. In contrast, too thin IMC layers would not be effective enough to offer sufficient connective strength, which is prone to the fracture at the joint interface. Therefore, research on the growth behaviors and thickness evolution of IMC at the interface of Sn1.0Ag0.5Cu solders will become the focus of this study. Firstly, in view of the urgent need for the solders of aerospace devices to serve at high temperature for a long period of time, an accelerated aging test in high temperature was carried out to evaluate their stability and usability. Secondly, the interfacial microstructures of Sn1.0Ag0.5Cu solder joints are analysed. Additionally, the growth mechanisms and laws of IMCs are explored. Finally, the numerical growth models of IMC bilayers are constructed.

2. Experimental

Sn1.0Ag0.5Cu solders are produced by Profound Material Technology Co. Ltd. The brazing was performed on Cu pads to form Sn1.0Ag0.5Cu/Cu structures. The analysis samples were prepared via sectioning, grinding and polishing. Metallographic test of micro-joints was carried out by optical microscope (DMR, Leica). The crystal structure was investigated using an X-ray diffractometer (X-ray diffraction，Rigaku D) applying Cu-K_α radiation source (λ=1.5406 Å) over a scanning range 2θ of 15°~75°. The melting points of solders were measured by differential scanning calorimeter (DSC 214 polymer, Netzsch). The temperature range was from 25 to 250 ℃ with a heating rate of 10 ℃/min. The microstructures of solder interfaces were observed by field emission scanning electron microscope (Meilin 6169, Zeiss), and elemental analysis was carried out by the energy dispersive X-ray spectroscopy (EDS) accessory of the microscope. Based on the microscopic SEM photos, the IMC area (*A*) and the length (*w*) of each interface layer were calculated by Image-J software. And the average thickness (*L*) of IMC at the interface was calculated according to formula (1). The schematic diagram for the measurement of *L* is displayed in figure 1.

$$L = \frac{A}{w} \quad (1)$$

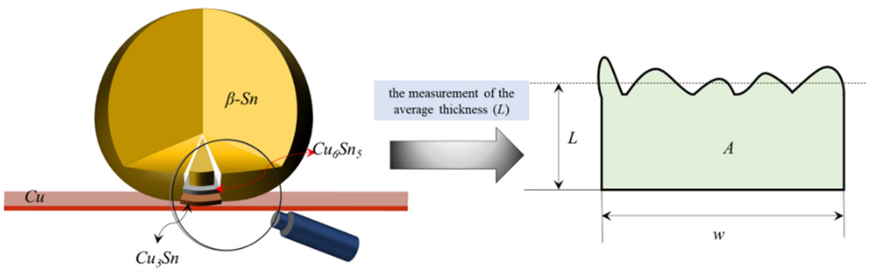

Figure. 1 Schematic diagram for the measurement of the average thickness (L)

3. Results and discussion

As shown in metallographic images (figure 2a), the solder alloys are mainly composed of β-Sn and eutectic phases. The eutectics consist of binary phases (Sn+Ag_3Sn、Sn+Cu_6Sn_5) and ternary phases (Sn+Ag_3Sn+Cu_6Sn_5). A slight amount of structural strengthening phases (Ag_3Sn) is sparsely distributed among β-Sn matrix. XRD pattern also demonstrates strong diffraction peaks of β-Sn and a weak peak of Ag_3Sn (figure 2b). During the welding, when the temperature was increased to 217~218 ℃, the transition of the eutectic ternary phases to liquid phase first occurs (Sn+Ag_3Sn+Cu_6Sn_5→liquid). After that, in the temperature range of 218~221 ℃, binary eutectic Sn/Ag_3Sn phases transit to liquid phase (Sn+Ag_3Sn→liquid). Elevating the temperature to 222~226 ℃, binary eutectic Sn/Cu_6Sn_5 phases transit to liquid phase (Sn+Cu_6Sn_5→liquid). At around 227 ℃, liquid phase transition of β-Sn occurs (β-Sn→liquid). These four transformation processes are suggested by four endothermic peaks on the DSC curve as shown in figure 2c. Chemical reactions occur between Sn and the welded metal during the welding of Sn1.0Ag0.5Cu solders. A thin IMC layer is formed at the interface. The SEM photos in figure 2d indicates that the initial IMC grains are scallop-like. It can be seen that Cu_6Sn_5 (η phase) is first generated at the interface through principal component analysis, as shown in figure 2e. It is noteworthy that the generation of Cu_6Sn_5 layer is the key to ensure the reliability of mechanical and electrical interconnection between solders and pads.

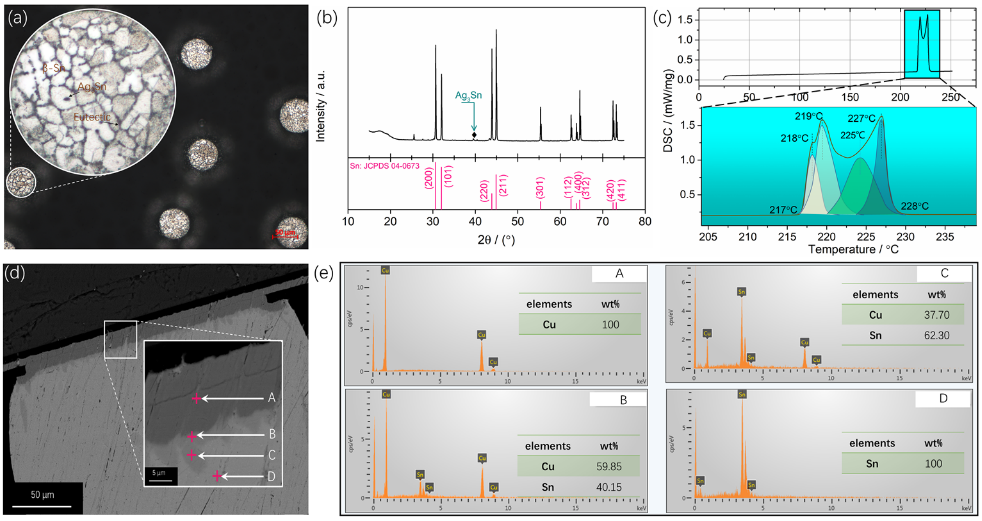

Figure 2. Characterizations of low silver lead-free Sn1.0Ag0.5Cu solders. (a) Metallographic images (b) XRD patterns (c) DSC thermograms (d) SEM photos (e) EDS analyses

When the solders are in service at high temperature for a long period of time, a Cu_3Sn (ε phase)/Cu_6Sn_5 (η phase) double-layer structure is developed with the extension of aging time (figure 3d). The aging rate of interfacial layers depends on the mutual diffusion rate of tin atoms and welded metal atoms. Since the tin atoms near the interface will gradually diffuse and migrate into the pad metals to form thicker IMC, resulting in reduction of the amount of tin at the interface, which is likely to pose a risk of embrittlement and cracking. Therefore, the interfacial IMC growth mechanisms and laws of Sn1.0Ag0.5Cu solders were explored. The interfacial reaction between Sn1.0Ag0.5Cu solders and pad metals is a dynamic process of IMC growth, pad metal consumption and solder matrix reducing. From figure 3a~h, it is proved that after long-period thermal storage of 200h, 700h and 1200h, the IMCs have changed from scallop-like monolayer to flattened bilayer, and the IMCs have gradually become thicker.

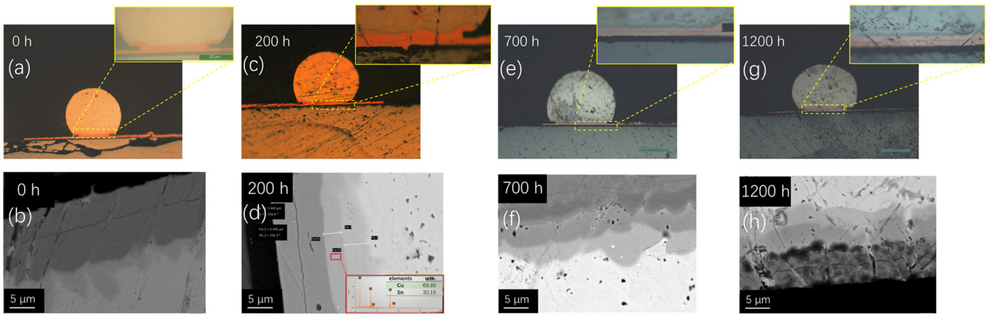

Figure 3. Optical and SEM photos of Sn1.0Ag0.5Cu micro-joints. (a)~(b) 0h (c)~(d) 200h (e)~(f) 700h (g)~(h) 1200h

The thickness of interfacial Cu_3Sn and Cu_6Sn_5 in Sn1.0Ag0.5Cu solder micro-joints at different thermal storage time is obtained through the formula (1). The results are shown in Table 1.

Table 1 The thickness of interfacial Cu_3Sn and Cu_6Sn_5 at different thermal storage time

IMC thickness (μm)	thermal storage time (h)			
	0	200	700	1200
Cu_3Sn	0	3.21	4.26	4.53
Cu_6Sn_5	2.34	3.40	3.85	4.08
total	2.34	6.60	8.11	8.60

In order to further understand the growth processes and mechanisms of interfacial IMCs (Cu_3Sn、Cu_6Sn_5), the growth kinetic parameters of IMCs were calculated by using the kinetic theoretical model. In addition, the growth mechanisms of IMCs were discussed. Although there are different mechanisms, the relationship between the IMC thickness (L) and aging time (t) can be expressed in a power exponential function, which are summarized as follows:

$$\Delta L(t) = Dt^n \tag{2}$$

There is a functional relationship between diffusion coefficient (D) and absolute temperature (T), which can be expressed by Arrhenius formula (3) [11].

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{3}$$

Where, D_0 is the constant, Q is the diffusion activation energy, and R is the gas constant.

Curves of lnΔL versus ln$t$ for Sn1.0Ag0.5Cu solder joints were linearly fitted, as shown in figure 4. Then, the fitted IMC growth kinetic parameters are obtained. To be specific, the growth kinetic equation of Cu_3Sn is expressed as equation: L (Cu_3Sn, μm) =0.223 $t^{0.20}$. While, the fitting equation for Cu_6Sn_5 is: L (Cu_6Sn_5, μm) =0.025 $t^{0.28}$+2.34. The growth of Cu_3Sn and Cu_6Sn_5 mainly controlled by grain boundary diffusion, and the average diffusion coefficient of metal atoms is 0.223 $\mu m^2 \cdot s^{-1}$.

From the developed numerical growth model of Cu_3Sn and Cu_6Sn_5 of Sn1.0Ag0.5Cu solder joints in figure 5, it is presented that "Cu+Sn→Cu_3Sn" reaction is more difficult than the "Cu+Sn→Cu_6Sn_5" reaction because of the requirement for higher initial activation energy in the early stage. Whereas, when the Cu_6Sn_5 layer is thickened to a certain extent, it is more difficult for Sn atoms to diffuse and pass through the thickened Cu_6Sn_5 layer leading to the supplies of free Sn atoms greatly reduced. Correspondingly, Cu_3Sn layer is so thin that Cu atoms can quickly diffuse to the interface and react with Cu_6Sn_5 layer (Cu_6Sn_5+Cu→Cu_3Sn). At this stage, Cu_3Sn tends to grow rapidly. On the contrary, the growth rate of Cu_6Sn_5 layer will gradually decrease. With the extension of aging time (critical time, 285 h), the growth thickness of Cu_3Sn layer exceeds that of Cu_6Sn_5 layer. But the growth rate of both layers decreases sharply. The possible reason is that the diffusion of free atoms at both ends needs to pass through the two thicker IMC layers, resulting in insufficient supply of free Sn and Cu atoms. It should be pointed out that the growth of Cu_3Sn mainly depends on the consumption of Cu_6Sn_5 (Cu_6Sn_5+Cu→Cu_3Sn). In other words, Cu_6Sn_5 is also consumed while growing. The thickness tends to stabilize when a balance of consumption and growth is reached. The growth of Cu_3Sn shows a similar trend. On the one hand, it is because the diffusion of atoms is limited. On the other hand, once Sn atoms pass through the Cu_6Sn_5 layer, Sn will react with Cu_3Sn (Cu_3Sn+Sn→Cu_6Sn_5). Hence, Cu_3Sn will also be consumed, and its growth rate will slow down.

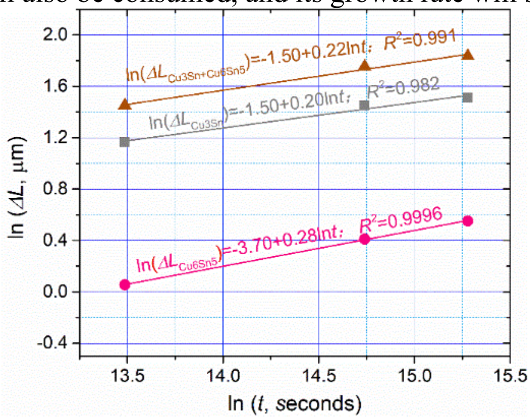

Figure 4. Fitting curves of lnΔL *vs.* ln$t$

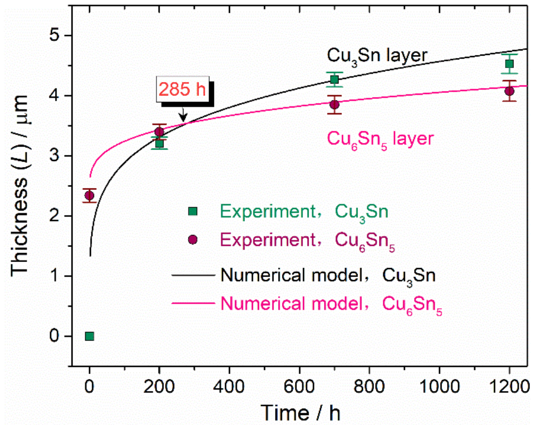

Figure 5. Growth curves of interfacial Cu_3Sn and Cu_6Sn_5 layers of Sn1.0Ag0.5Cu solder joints

4. Conclusion

In this paper, the microstructures of low silver lead-free Sn1.0Ag0.5Cu solders with different aging time at 150°C were investigated. The growth mechanisms and thickness evolution laws of interfacial IMCs (Cu_6Sn_5 and Cu_3Sn) were explored. The growth kinetic equations for Cu_6Sn_5 and Cu_3Sn layers are obtained, respectively. The equations are following: L(Cu_6Sn_5, μm)=0.025 $t^{0.28}$+2.34, L(Cu_3Sn, μm)=0.223 $t^{0.20}$. The experimental data is in good agreement with the constructed numerical model. The research results might provide references for lifetime analysis and reliability evaluation of low silver lead-free solder used in high temperature environment.

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