Effect of Trace Cu on Microstructure, Spreadability and Oxidation Resistance Property of Sn-xCu Solders

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Sn-xCu (x = 0.5, 0.7, 0.9, 1.1, 1.3) solders were prepared to investigate the influence of trace Cu on the microstructure, the spreadability and the oxidation resistance property of Sn-xCu lead-free solder. Researches have shown that the Cu content had a significant impact on the microstructure, the microstructure of Sn-0.7Cu solder was almost fine dendrites and others were composed of coarser dendrites. The liquidus temperatures of Sn-xCu were around 227°C; the peak of solidification temperature had vast difference and the biggest difference was 8.8°C. The peak of solidification temperature of Sn-0.7Cu was the smallest, with 192°C. The spreading rate of Sn-xCu solders greatly improved, in which Sn-0.5Cu improves by nearly 4 percent, Sn-0.7Cu improves by nearly 3 percent and the others improve by 2 percent around from 260°C to 290°C. With the increase of Cu content, there were no obvious changes to solder with wetting power and wetting time, interfacial IMC thickness of Sn-xCu/Cu solders. The color of oxidation film deepened due to the serious oxidation with the increase of the temperature. The oxide slag of Sn-xCu solders decreased and then increased with the increase of Cu content, in which the oxide slag of Sn-0.7Cu solder was the lowest, about 18.5% of Sn-0.5Cu and 38% of Sn-1.3Cu. 

1. Introduction

The lead-free progress of electronics greatly promotes the development of lead-free solders and the relevant soldering technology. It is known that the best alloy instead of Sn-Pb solders is a eutectic alloy comprising of Sn, Ag and Cu in the study of lead-free solders.1–2 Since eutectic Sn-Ag and Sn-Ag-Cu is rich in silver that is expensive in price, resulting in increased manufacturing cost of electronics, eutectic Sn-Ag and Sn-Ag-Cu is severely restricted for popularization and application. While, Sn-Cu alloy is regarded as the most cost-effective lead-free solder that is widely used for wave soldering on account of abundant sources and low price.

In recent years, many domestic and overseas scholars have done a comprehensive research on wettability, interface compounds,1–5 surface tension,6 melt structure and viscosity,7,8 electromigration9 of eutectic alloy Sn-0.7Cu. Since Sn-0.7Cu lead-free solder is poor in wettability and spreading property for metal substrate and easily oxidized in application,10 some elements such as Pd, Cr, Cu11), Ag, In12), Al13,14), Bi15,16), Ni17–19) and nanoparticle20,21) had been added into Sn-0.7Cu solders to improve its comprehensive performance, which achieved good research results. While, the pins of component got serious copper corrosion, leading to changes of solder compositions in wave soldering process, which made substantial changes to the performance of Sn-0.7Cu solder. Wang Lai22,23) and Fei-Yi Hung24) only had studied the effect of Cu content on interfacial IMC and microstructure of solders, but lacking in systematic studies on wettability, solidified characterization, oxidation resistance property of solders with Cu content. Meanwhile, the results are difference between the present studies and our study, for example, the thickness change of IMC with the increase of Cu content23) and the morphologies of Cu6Sn5 IMCs in the solder alloys25–27).

Therefore, this paper gives a comprehensive research on microstructure, melting characteristic, solidified characterization, flowability, wettability, interfacial IMC and oxidation resistance property of Sn-xCu solders with Cu content.

2. Experiment and Method

Five Sn-xCu solders (x = 0.5, 0.7, 0.9, 1.1, 1.3, respectively) were prepared with Sn and Cu in 99.9% purity according to stoichiometric ratio using temperature control solder stove at 450°C in protective atmosphere. A sample of 2–3 mg was taken for heating up from 190°C to 250°C at 1°C/min and then cooling at the same speed using Q20 differential scanning calorimeter provided by American TA company. The solders were completely melted and uniformly mixed with temperature preservation for 3 minutes at 275°C, then taken out for cooling under atmospheric temperature. And the microstructure of solders was observed using Leica DM2500M upright metallurgical microscope and the phase analysis was carried out by DX2500 x-ray diffractometer. Taking JIS-Z-3198 for reference, the spreading test of solders at 260°C, 275°C and 290°C respectively was carried out with copper sheet of 30 mm × 30 mm × 0.3 mm after polished using and aged at 150°C for 1 hour, Sn-xCu solder ball of 0.2 g (x = 0.5, 0.7, 0.9, 1.1, 1.3, respectively), and rosin flux which comprised of 2.5 g rosin, 7.5 g isopropyl alcohol and 0.229g dimethylamine hydrochloride. Later, the intermetallic compounds (IMC) layer of these samples in the spreading test was observed using SUPRA55 thermonic field emission scanning electron microscope. The solderability of Sn-xCu solders was tested with copper sheet of 30.0 mm × 5.0 mm × 0.3 mm, providing immersing speed of 2 mm/s and immersing depth of 3.0 mm for 5 minutes using SAT-5100 solderability checker and rosin flux (same as above) at 260°C, 275°C, 290°C respectively. The molten solders were put into the tin melting stove with inner diameter of 33.5 mm with tempera-
ture preservation for 30 minutes at 260°C, 275°C and 290°C respectively, to visually observe the changes on surface color of molten solders and collect the oxide slag within 30 minutes.

3. Results and Discussion

3.1 Effect of Cu content on microstructure of Sn-xCu solders

Figure 1 (a) shows the phase analysis of Sn-xCu solders, and it is noted that Sn-xCu solders substrate is comprised of β-Sn and Cu₆Sn₅ and the peak of Cu₆Sn₅ becomes much significant with the increase of Cu content. Figure 1(b)-(f) shows the microstructure of Sn-xCu solders, and it is indicated that the change of Cu content results in obvious changes to the microstructure of Sn-xCu solders, in which Sn-0.5Cu is coarse dendrite, Sn-0.7Cu is fine coarse dendrite and Sn-(0.9-1.3)Cu is coarser dendrite. From Fig. 2, Sn-1.1Cu solder is mainly comprised of primary crystal β-Sn, eutectic structure of β-Sn+Cu₆Sn₅ and H-shape Cu₆Sn₅, and there are many Y-shape and bird-like shape, E-shape and I-shape Cu₆Sn₅ in Sn-1.3Cu solder. The stubby Cu₆Sn₅ may be the cause of solder structure coarsening, and the coarse dendritic microstructure may be the cause of fracture and decreased mechanical performance to soldering joints. The literatures (24,25) have found that the structure of solders is changed from fine coarse to coarse dendrite when Cu content is more than 0.7%. Cu₆Sn₅ is stubby H shape when the Cu content reaches to 1.1%, and Cu₆Sn₅ is more stubby H shape when the Cu content reaches to 1.4% (25). The morphologies of Cu₆Sn₅ IMCs in the solder alloys were I-like, Y-like and bird-like shapes (26,27). As reported in the references (28) that Cu₆Sn₅ had two crystal structures.

According to Cu-Sn phase diagram, as the temperature decreases from the melting point to 186°C, an allotropic transformation of Cu₆Sn₅ may change from hexagonal structure (η-phase) to monoclinic structure (η'-phase). (29) It drew a conclusion that these Cu₆Sn₅ IMCs are η'-phase because the temperature (room temperature) is below 186°C. Three Ag₃Sn growth patterns were also observed, i.e., linear (half-line) shape, Y shape and (V) shape, which were also primarily related to the crystal structure of Ag₃Sn which is a close-packed hexagonal structure. (30) Besides, the different shapes of Cu₆Sn₅ maybe caused by polished using abrasive paper.

Figure 3 and Table 1 shows curves and characteristics of the melting and solidification of Sn-xCu solders at the speed of 1°C/min, and it is noted that the peak melting temperature of Sn-xCu solders is all between 226.6°C and 227.3°C, that is the transformation from Sn+Cu₆Sn₅ to liquid, which is basically identical with theoretical eutectic temperature of Sn-0.7Cu, having no obvious solidus-liquidus temperature difference. For Sn-0.5Cu, one of the melting peak is solids

![Fig. 1 XRD and microstructure of Sn-xCu solders. (a) XRD; (b) Sn-0.5Cu; (c) Sn-0.7Cu; (d) Sn-0.9Cu; (e) Sn-1.1Cu; (f) Sn-1.3Cu.](image)

![Fig. 2 Micrograph of Cu₆Sn₅ in Sn-1.1Cu (a) and Sn-1.3Cu (b) solder.](image)

![Fig. 3 Curves of the melting (a) and solidification (b) of Sn-xCu solders.](image)
temperature and one of the melting peak is liquidus temperature at 226.6°C. The changes of Cu provide big effect on the solidification temperature of Sn-xCu solders, and with only one eutectic transformation peak that is achieved at 192°C for Sn-0.7Cu and Sn-1.3Cu, at around 200.5°C for Sn-0.9Cu and Sn-1.1Cu, at around 198.3°C for Sn-0.5Cu, i.e. Sn-1.1Cu > Sn-0.9Cu > Sn-0.5Cu > Sn-0.7Cu > Sn-1.3Cu, with the maximum temperature difference of 8.8°C. The literature²⁵ has found that the size of Cu₆Sn₅ conformed to the rule of Sn-1.4Cu > Sn-2.1Cu > Sn-0.4Cu > Sn-0.1Cu > Sn-0.7Cu and the size of primary crystal β-Sn conformed to the rule of Sn-1.4Cu > Sn-2.1Cu > Sn-0.4Cu > Sn-0.1Cu > Sn-0.7Cu (decreased firstly and then increased and decreased) as Cu content increased at a certain cooling temperature (1°C/min). In this research, the size of Cu₆Sn₅ and primary crystal β-Sn of Sn-1.3Cu are also bigger than the size in Sn-1.1Cu. During the solidification progress, non-eutectic solders firstly separated out primary crystal β-Sn and then eutectic structure of β-Sn+Cu₆Sn₅ after reached eutectic composition.

The nucleation undercooling of Sn-xCu solders are about 30 ± 4°C, which means that the presence of primary Cu₆Sn₅ has no significant effect on the nucleation undercooling of β-Sn, which suggests that primary Cu₆Sn₅ crystals are not catalytic sites for β-Sn nucleation.³¹

### 3.2 Effect of Cu content on flowability of Sn-xCu solders

The density of Sn-xCu solders and the diameter of 0.2 g solder ball are calculated based on the density of Sn and Cu. The spreading rate of solder is calculated using the following eq. (1) based on the height H for various solders measured in spreading experiment. The spreading rate of Sn-xCu solders respectively is given in Table 2.

\[ S_R = \left( D - H \right)/D \times 100\% \quad (1) \]

Where, \( S_R \) is the spreading rate (%), \( D \) is the diameter of ball when see the solder as a ball, \( D = 12.4V^{1/3} \), \( V \) is the volume of solder in the experiment and \( H \) is the height of solder after spreading.

When the temperature comes up from 260°C to 290°C, the spreading rate of Sn-xCu solders significantly increases, which is going down as Cu content increases, providing a higher spreading rate by nearly 4 percents for Sn-0.5Cu, 3 percents for Sn-0.7Cu and 2 percents for other solders. At the same temperature, the spreading rate goes up and then goes down with the increase of Cu content, among which the spreading rate of Sn-0.7Cu is the biggest one with 77.47% at 290°C.

The spreading behavior of solder is a melt flowing process with wet surface based. On the premise of constant solder, temperature and copper sheet, the spreading rate mainly depends on two factors, in which one is low surface tension to get wet surface and the other one is low viscosity to provide better flowing performance. The less surface tension, the better flow property, and the solder would be easier to spread. The relationship between surface tension \( \sigma \) of liquid solder and the temperature T is as given by equation follows:⁷–⁹

\[ \sigma = \frac{k(T_c - T - 6K)}{(m\rho)^{1/2}} \quad (2) \]

Where, \( m \) is the molar mass of liquid, \( \rho \) is the liquid density, \( k \) is the empirical constant and \( T_c \) is the critical temperature with surface tension being zero. The relationship between the melt viscosity \( \eta \) and the temperature T of molten metal can be generally described by the Arrhenius equation:⁷–⁹,²⁵

\[ \eta = \frac{h}{V_m} \exp\left( \frac{e}{kT} \right) \quad (3) \]

Where: \( \eta \) is the viscosity, \( H \) is the Planck constant, \( V_m \) is the flow unit (ion, atom or cluster) size, \( e \) is the flow activation (i.e. activation energy required for flow unit to move from one equilibrium position to another), \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

Thus, the surface tension \( \sigma \) of solder would decrease and the viscosity of melt would decrease exponentially as the temperature increases, which is conducive to wetting and spreading behaviors of solder. Zhao Ning⁶–⁸ also have found that the viscosity and the surface tension of Sn-xCu (\( x = 0.7, 1.5, 2 \)) decreased and the viscosity and surface tension of Sn-xCu solders increased with the increase of temperature in low temperature zone.

Przemysław’s calculation shows that the surface tension of Sn-xCu solders significantly changes with various Cu contents at 1373 K when Cu content increases to 0.5%,²⁵ the surface tension increases by over 10% when Cu content increases to 0.7%. The surface tension increases by more than one time when Cu content increases to 1%. Table 3 gives the wettability data of Sn-xCu solders at 275°C, indicating the wettability decreases and the surface tension increases as Cu content increases. By comparing with the microstructure in Fig. 1, it is found that the solder is clear dendrite structure with good flowability that is better as more close to eutectic when Cu content is less than 0.7%, and the intermetallic compound (IMC) increases when Cu content is more than 0.7%, so does the viscosity. Therefore, under a certain temperature,
the surface tension of solder would increase and the viscosity of melt would first decrease and then increase as Cu content rises, and the spreading rate would first increase and then decrease accordingly under the combination of two above, which is identical with the measurement results in literature7,8).

Figure 4 shows the microstructure of Sn-xCu/Cu solders after spreading for 30 s at 275°C. The thickness of Sn-xCu/Cu solders has no obvious change as Cu content increases. The interfacial IMC shape looks like needle-type as shown in Fig. 4 (a) and (b), because the copper content in the solders are too small at the formation of IMC during the soldering process which cause the IMC ingrown. Hereafter, the interfacial IMC become flat. While, the bulk IMC in the solders close to the interfacial significantly increases as Cu content rises, and IMC in Sn-1.3Cu is the most obvious.

3.3 Effect of Cu content on oxidation resistance property of Sn-xCu solders

Table 4 shows the surface state of after oxidation for 30 minutes under 260°C, 275°C and 290°C. The thickness of Sn-xCu/Cu solders is deep yellow and then turns to light yellow and turns back to deep yellow at last with the increase of Cu content. At the temperature of 290°C, the oxidation film of Sn-xCu solders is deep grey and then turns to light grey and turns back to deep grey at last with the increase of Cu content.

At lower temperature, the main compound on the surface layer of Sn-xCu solders is SnO2 since Sn is much easy to get oxidized as the temperature rises. At the temperature of 260°C, the oxidation film of Sn-xCu solders is deep yellow and then turns to light yellow and turns back to deep yellow at last with the increase of Cu content. At the temperature of 290°C, the oxidation film of Sn-xCu solders is deep grey and then turns to light grey and turns back to deep grey at last with the increase of Cu content.

Table 5 shows the surface oxide film mass of Sn-xCu solders after holding the temperature for 30 minutes. With Cu content kept the same, the solder oxide slag is apt to drop but in a small amount as the temperature rises, which is because that the flow property of solders increases and pure tin in the oxide slag decreases as the temperature rises. From the average value of oxide slag, at the same temperature, the oxide slag of Sn-xCu solders increases with the
increase of Cu content, which decreases firstly and then increases, and among them the average oxide slag of Sn-0.7Cu solder is the lowest, about 18.5% of Sn-0.5Cu, 38% of Sn-1.3Cu and 2/3 of Sn-(0.9–1.1)Cu. The more far away from eutectic point, the more oxide slag of Sn-xCu solders, which is because of the oxide slag containing tin due to poor flowability, and also may be because of the oxidation film compactness getting worse due to changes of Cu content, which will be further studied.

4. Conclusions

(1) It was found that the change of trace Cu content resulted in obvious changes to the microstructure of Sn-xCu solders, in which Sn-0.5Cu was coarse dendrite, Sn-0.7Cu was fine coarse dendrite and Sn-(0.9–1.3)Cu was coarser dendrite. The peak melting temperature of Sn-xCu solders was all between 226.6°C and 227.3°C. The peak solidification temperature of Sn-0.7Cu and Sn-1.3Cu was about 192°C, in which Sn-0.9Cu and Sn-1.1Cu gets solidification at 200.5°C, Sn-0.5Cu got solidification at 198.3°C, having peak solidification temperature difference of 8.8°C at most.

(2) When the temperature was increased from 260°C to 290°C, the spreading rate of Sn-xCu solders greatly improved, in which Sn-0.5Cu improves by nearly 4 percents, Sn-0.7Cu improves by nearly 3 percents and the others improve by 2 percents around. At the same temperature, the spreading rate increased firstly and then decreased as Cu content increased, and Sn-0.7Cu was one of the biggest. With the increase of Cu content, there were no obvious changes to solder with wetting power and wetting time, interfacial IMC thickness of Sn-xCu/Cu solders.

(3) With the increase of temperature, the surface oxidation film of Sn-0.5Cu was deep yellow and then became grey and turn to brown, and the surface oxidation film of Sn-0.7Cu was light yellow and then became grey and turn to deep grey. The oxide slag of Sn-xCu solders decreased and then increased with the increase of Cu content, in which the oxide slag of Sn-0.7Cu solder was the lowest, about 18.5% of Sn-0.5Cu and 38% of Sn-1.3Cu.

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