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Materials

Effect of Ag and Ni on the melting point and solderability of SnSbCu solder alloys

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Abstract: To improve the properties of Sn10Sb8Cu solder alloy, two new solders (SnSbCuAg and SnSbCuNi) were formed by adding small amounts of Ag or Ni into the solder alloy. The results show that the melting point of the SnSbCuAg solder alloy decreases by 14.1°C and the spreading area increases by 16.5% compared to the matrix solder. The melting point of the SnSbCuNi solder alloy decreases by 5.4°C and the spreading area is slightly less than that of the matrix solder. Microstructure analysis shows that adding trace Ag makes the melting point decline due to the dispersed distribution of SnAg phase with low melting point. Adding trace Ni, Cu_6Sn_5 and $(Cu, Ni)_6Sn_5$ with polyhedron shape on the copper substrate can be easily seen in the SnSbCuNi solder alloy, which makes the viscosity of the melting solder increase and the spreading property of the solder decline.

Key words: solder alloy; Ag; Ni; melting point; solderability

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1. Introduction

Because of excellent performances such as low melting point, excellent mechanical properties and low price, the traditional SnPb solder is extensively used as an electronic material in the modern electronic manufacturing industry, particularly household appliances, electronic communications and other related electronic industries. However, lead and its compounds are toxic substances which bring great security risks to the environment and human life. Many countries have gradually adopted legislation to restrict or even prohibit the use of lead in electronic industries. China has also promulgated the "approach to pollution prevention and management of electronic and information products" to limit the use of lead-contained solders. It has been urgent for researching and developing new lead-free solder materials as the replacement of SnPb solder.

In recent years, research works about lead-free solders have a swift development [1-6]. At present, dozens of lead-free solder alloys, such as SnSb, SnAg, SnCu, SnBi and SnZn series, had been developed. However, the thermal conductivity, reliability and solderability of the SnSb binary solder alloy are worse than those of SnAg solder and SnCu solder. Studies about adding trace or adding appropriate third, fourth elements into the above binary solder alloy to form new multielement alloys had been carrying through. SnSbCu solder alloy drew well attention because it had been widely applied for its low cost and high reliability in multi-chip packaging, semiconductor device and the I/O pins with multi-layer ceramic substrate connections [7-12]. Lee's study [13] showed that no ternary phase existed in the SnSbCu alloy, and the reliability of SnSbCu was better than that of the SnSb binary solder. Jan Hu, *et al.* studied the wettability, microstructure and melting point of the SbSnCu (Bi) lead-free solder, and the results showed that adding Bi in the SbSnCu solder alloy could reduce the melting point and improve the spreadability, but the distance of the liquid-solid two-phase section of the solder alloy increased and its mechanical properties were poor [14]. In the present work, two new quadru-

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ple lead-free solders (SnSbCuAg and SnSbCuNi) were formed by adding small amounts of Ag or Ni into Sn10Sb8Cu ternary solder alloy. The influences of Ag and Ni on the melting point, spreadability and microstructure of the new solder alloys were investigated.

2. Experimental procedure

2.1. Solder preparation

The pure Sn, Sb, Ag, Ni and Cu with purity of 99.95% were used as raw materials. The compositions of the investigated alloy are shown in Table 1. The allowable error is ±1wt%. The solder alloys were made in a non-consumable arc furnace for 30 min under the vacuum of 5×10^{-2} Pa. To guarantee uniformity of the alloy, the solders were overturned 3 times.

Table 1. Composition of the examined solder alloy wt%

No.	Sn	Sb	Cu	Ag	Ni
1	82	10	8	0	0
2	82	10	8	1	0
3	82	10	8	0	1

2.2. Physical properties testing

The melting temperature of the solder alloy was measured with differential scanning calorimeter (DSC). The sample for the DSC analysis was a piece of about 15 mg solder. The scanning temperature was set from 0 to 1000°C with a heating rate of 10°C/min under Ar atmosphere.

2.3. Spreading properties testing

In the spreading properties test, copper sheets with dimensions of 40 mm×40 mm×0.2 mm were polished using 400 grit sand paper and washed in methyl alcohol. The solder of 0.2 g ±1% was plated on the Cu sheets. Soldering was conducted on a computer controlled re-flow machine. The soldering process was carried out at 350°C for 5 min. After soldering, the specimen was cleaned with acetone to remove the leftover of flux. The specimen was scanned into a computer along with an area-preknown reference and the spreading area of the solder was calculated through the function of “inquire” in AutoCAD software. The spreading sample was sectioned along the center of the spreading solder metal and the specimen fracture profile was scanned and copied into AutoCAD software, then the wetting angle of the solder was calculated through the function of “labeling angle” in AutoCAD software as shown in Fig. 1.

The angle θ can be calculated by the formula as follows:

$$\theta = \frac{\theta_L + \theta_R}{2} \tag{1}$$

where θ is the wetting angle, θ_L the left wetting angle and θ_R the right wetting angle.

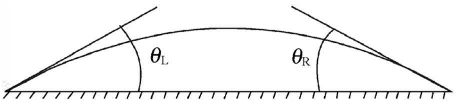

Fig. 1. Wetting angle.

2.4. Microstructure observation

The sample was inserted into two copper sheets and fixed with 502 glue, polished with metallographic water sand paper and 2.5 μm carborundum polishing paste, and corroded with 4vol% of HNO_3 alcohol solution for 5 s. The microstructure was observed with a JSM-5610LV scanning electron microscope, and the phases were analyzed using EDAX and D8-Advance X-ray diffraction.

3. Results and discussion

3.1. Effect of Ag and Ni on the melting temperature of the SnSbCu solder

The solidus temperatures, liquidus temperatures and the melting points of Sn10Sb8Cu1Ag, Sn10Sb8Cu1Ni and Sn10Sb8Cu are shown in Fig. 2. It can be seen that the solidus temperature, melting point and liquidus temperature of Sn10Sb8Cu1Ag solder are 220.5, 236 and 238.2°C, respectively, which is 18.3, 14.1 and 22°C lower than those of Sn10Sb8Cu solder alloy, respectively. The width of liquid and solid two-phase region temperature of Sn10Sb8Cu1Ag is also reduced by 3.7°C.

The effects of Ni on the solidus temperature, liquidus temperature and melting point of the SnSbCu solder alloy are similar to those of Ag. It can be seen from Fig. 2 that the solidus temperature, melting point and liquidus temperature of the Sn10Sb8Cu1Ni solder decline by 4.6, 5.4 and 4.1°C respectively compared with those of the SnSbCu solder. But the width of the liquid and solid two-phase region temperature is almost remained.

Fig. 3 is the SEM images of Sn10Sb8Cu, Sn10Sb8Cu1Ag and Sn10Sb8Cu1Ni solder. Energy spectrum analysis shows that the microstructure of Sn10Sb8Cu is composed of gray SnSbCu ternary solid solutions, irregular strips of atramentous Cu_6Sn_5 and Cu_3Sb, and blocks of dark gray SnSb binary phase. Adding 1% Ag into Sn10Sb8Cu solder alloy, SnAg phase is found in Sn10Sb8Cu1Ag solder alloy except grey SnSbCu solid solution, Cu_6Sn_5, Cu_3Sb and SnSb. The melting point of SnAg (about 221°C) is lower than that of Sn10Sb8Cu. The existence of the low melting point phase may be the reason for the declining of the solidus temperature, melting point and liquidus temperature of Sn10Sb8Cu1Ag quaternary alloy. The statistical results show that the area percents of the black irregular strips Cu_6Sn_5 and Cu_3Sb in Sn10Sb8Cu and Sn10Sb8Cu1Ag solder alloys are 15.3% and 12.8%, respectively. That is to say Cu_6Sn_5 and Cu_3Sb in Sn10Sb8Cu1Ag solder alloy are slightly reduced than those in the matrix solder (as shown in Fig. 3(a) and (b)). Since the melting points of Cu_6Sn_5 and Cu_3Sb are 415 and 586°C respectively, the decreasing of those high melting point phases maybe causes the decreasing of the melting temperature of Sn10Sb8Cu1Ag solder alloy.

The microstructure of Sn10Sb8Cu1Ni solder is also composed of gray SnSbCu ternary solid solutions, irregular strips of atramentous Cu_6Sn_5 and Cu_3Sb and blocks of dark gray SnSb binary phase. Ni exists in needle-like $NiSb_2$ in SnSb phase. But the shape of the low melting point phase SnSb (about 250°C) is changed from irregular shape to lump and the area percents reduces. The shape of the high melting point phase Cu_6Sn_5 and Cu_3Sb is changed from rod to irregular round or oval-shape and the area percents slightly decreases, which also makes the melting point of Sn-10Sb-8Cu solder alloy decreased.

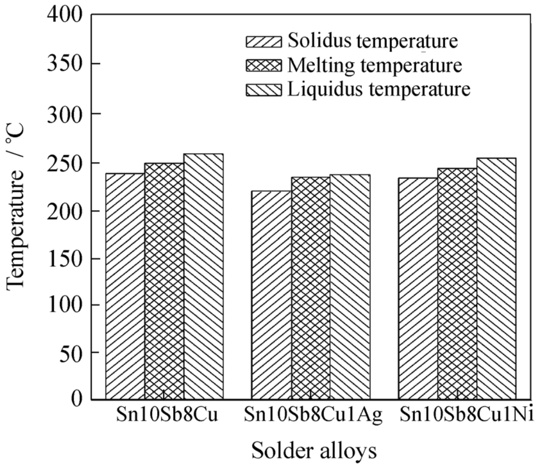

Fig. 2. Melting temperature of solder alloys.

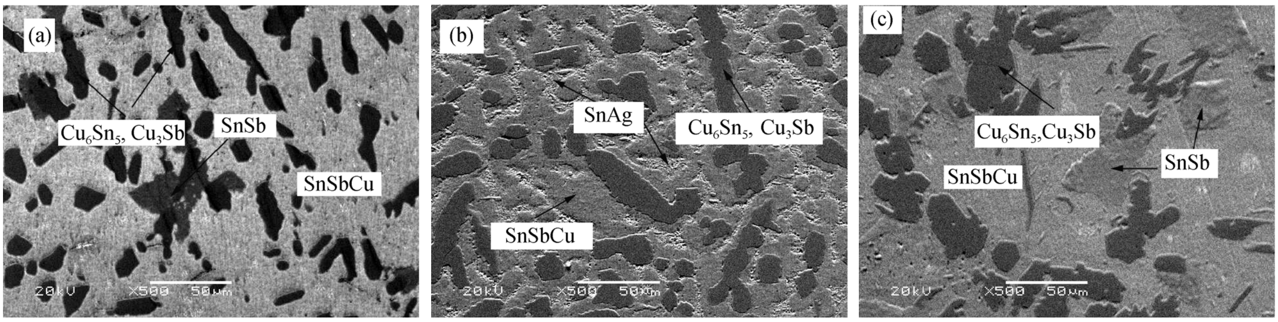

Fig. 3. SEM micrographs of solder alloys: (a) Sn10Sb8Cu; (b) Sn10Sb8Cu1Ag; (c) Sn10Sb8Cu1Ni.

3.2. Effects of Ag and Ni on the spreadability of the SnSbCu solder

The spreading areas and wetting angles of Sn10Sb8Cu solder, Sn10Sb8Cu1Ag and Sn10Sb8Cu1Ni are shown in Fig. 4. It can be seen that the spreading area of Sn10Sb8Cu1Ag solder increases by 19.4% and the wetting angle decreases by 3.75° than those of the matrix solder under the same soldering process, while the spreading area and wetting angle of Sn10Sb8Cu1Ni also decreases by 10.7% and increases by 1° respectively compared with those of the matrix solder. It clearly indicates that adding 1% Ag can improve the spreadability of Sn10Sb8Cu solder alloy, while adding 1% Ni makes the spreadability of Sn10Sb8Cu decrease.

Seen from Fig. 2, the melting point of Sn10Sb8Cu1Ag solder alloy is 14.1°C lower than that of the SnSbCu solder alloy. Under the same soldering process, the overheating temperature of Sn10Sb-8Cu1Ag solder alloy is higher than that of the matrix solder. Generally, the higher overheating temperature, the better the fluidity of the solder alloy, then the larger the spreading area and the smaller the wetting angle [15]. Therefore, the spreadability of Sn10Sb-8Cu1Ag solder alloy is better than that of the matrix solder. The width of the liquid and solid two-phase region temperature affects its spreadability to a certain extent. A larger width resulting in the improvement in viscosity of the melting solder is bad for its spreadability. Seen from Fig. 2, the liquid and solid two-phase region temperature widths of Sn10Sb8Cu and Sn10Sb8Cu1Ag solder alloys are 21.4 and 17.7°C, respectively. This is to say, adding small amounts of Ag into the matrix solder alloy can reduce the liquid and solid two-phase region temperature width, which indicates that Sn10Sb8Cu1Ag has a better spreadability than the matrix solder.

The spreadability of the solder alloy is related to the thickness and shape of the substrate intermetallic compounds. The more irregular the shapes of the substrate intermetallic compounds, the worse the spreading performance of the solder alloy, the slight metallurgical reaction between the solder alloy and the substrate can promote the spreading property of the solder alloy. [16]. The SEM images of the substrate intermetallic compounds of Sn10Sb8Cu, Sn10Sb8Cu1Ag and Sn10Sb8Cu1Ni solders are shown in Fig. 5. The statistical results show that the substrate intermetallic compound thicknesses of Sn10Sb8Cu1Ag and the matrix solder are 3.8 and 3.1 μm, respectively. So the spreadability of Sn10Sb8Cu1Ag solder is better than that of the matrix solder.

The effect of Ni on the spreadability of Sn10Sb8Cu solder alloy is different from that of Ag. The melting point and liquidus temperature of Sn10Sb8Cu1Ni hardly change compared with those of Sn10Sb8Cu solder. But there is a greater impact on the substrate intermetallic compound thickness. The solder alloy reacts too strenuous with the substrate so that the substrate intermetallic compound thickness are too thick, which is negative for the spreading of the solder alloy [16]. The statistical results show that the substrate intermetallic compound thickness of Sn10Sb8Cu1Ni solder is 7.6 μm, which is about double of the substrate intermetallic compound of the matrix solder. Energy spectrum analysis shows that the substrate intermetallic compounds of Sn10Sb8Cu1Ni solder are composed of Cu_6Sn_5 and polyhedron $(Cu, Ni)_6Sn_5$. Cu_6Sn_5 is covered by $(Cu, Ni)_6Sn_5$. And a large number of intermetallic compounds are found on the copper substrate which results in the increase of viscosity and the significant decrease of the spreadability of Sn10Sb8Cu1Ni solder alloy.

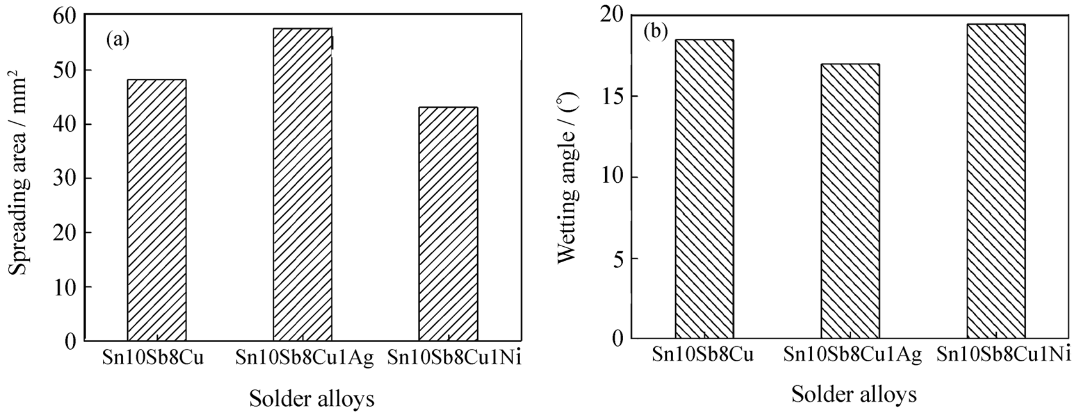

Fig. 4. Spreadability of solder alloys on copper substrates: (a) spreading area; (b) wetting angle.

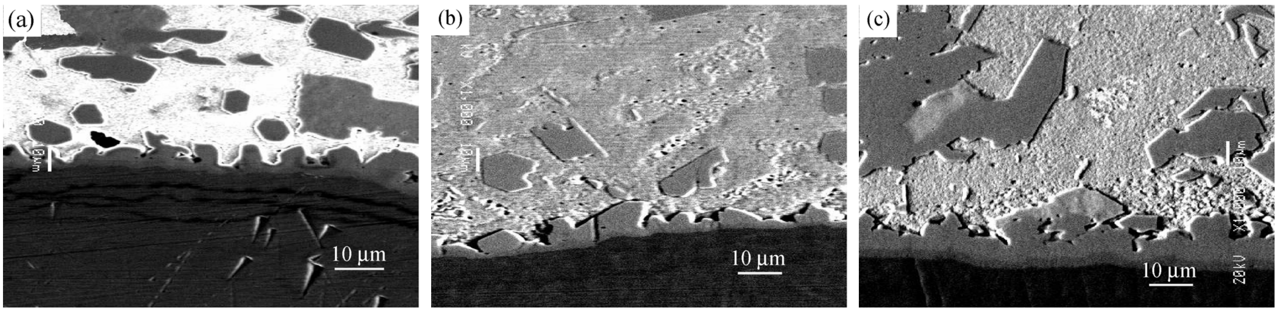

Fig. 5. Intermetallic compounds in Cu substrates: (a) Sn10Sb8Cu; (b) Sn10Sb8Cu1Ag; (c) Sn10Sb8Cu1Ni.

4. Conclusions

(1) Small amounts of Ag or Ni have different affects on the melting point of Sn10Sb8Cu solder. The solidus temperature, melting point and liquidus temperature of Sn10Sb8Cu1Ag solder alloy decrease by 18.3, 14.1 and 22°C respectively compared with those of Sn10Sb8Cu solder alloy, and the width of the liquid-solid phase range reduces by 3.7°C. But the solidus temperature, melting point and liquidus temperature of Sn10Sb8Cu1Ni solder alloy hardly change, and the width of the liquid-solid phase range slightly increases.

(2) Small amounts of Ag or Ni have great impact on the spreadability of Sn10Sb8Cu solder. The spreading area and the wetting angle of Sn10Sb8Cu1Ag solder increase by 19.4% and decreased by 3.75° respectively compared with those of Sn10Sb8Cu solder alloy. But the spreading area and the wetting angle of Sn10Sb8Cu1Ni solder decrease by 10.7% and increase by 1° respectively compared with those of Sn10Sb8Cu solder alloy. It is clear that adding 1% Ag can improve the spreadability of Sn10Sb8Cu solder alloy, but adding 1% of Ni results in the spreadability of Sn10Sb8Cu1Ni dropping.

(3) The effect of Ni on the spreadability of Sn10Sb8Cu solder alloy is different from that of Ag. Adding Ag into the SnSbCu solder makes the solderability of the matrix solder increase, while adding Ni into SnSbCu solder has the opposite effect. It is related to the shape and thickness of the substrate intermetallic compound.

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