Evaluation on the Characteristics of Tin-Silver-Bismuth Solder

Z. Xia, Y. Shi, and Z. Chen

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Tin-silver-bismuth solder is characterized by its lower melting point, good wetting behavior, and good mechanical property for which it is expected to be a new lead-free solder to replace tin-lead solder. In this article, Sn-3.33Ag-4.83Bi solder was investigated concerning its physical, spreading, and mechanical properties under specific conditions. Cooling curves and DSC results showed that it was close to eutectic composition (m.p. 210°-212 °C). Coefficiency of thermal expansion (CTE) of this solder, between that of PCBs and copper substrates, was beneficial to alleviate the thermal mismatch of the substrates. It was also a good electrical and thermal conductor. Using a rosin-based, mildly activated (RMA) flux, a spreading test indicated that SnAgBi solder paste had good solderability. Meanwhile, the solder had high tensile strength and fracture energy. Its fracture mechanism was a mixture of ductile and brittle fracture morphology. The metallographic and EDAX analyses indicated that it was composed of a tin-based solid solution and some intermetallic compound (IMC) that could strengthen the substrate. However, these large needle-like IMCs would cut the substrate and this resulted in the decreasing of the toughness of the solder.

Keywords mechanical property, physical property, spreading behavior, tin-silver-bismuth solder

1. Introduction

Tin-lead solder has been used widely for nearly a half millennium for its good solderability. However, ever-increased environmental consciousness drives people to develop new lead-free solder. Many lead-free solders have been developed since the 1990s, but the “drop-in” product still doesn’t exist.[1-6] However, some special solder with special application does exist. Tin-silver-bismuth solder is characterized by its lower melting point, good wetting behavior, and good mechanical property. It is expected to be a new lead-free solder to substitute for tin-lead solder. There have been some reports on the Sn-Ag-Bi solder.[7,8] However, data were not clear because of lack of comparability for some experimental conditions in these articles. Furthermore, comprehensive tests of physical, mechanical, and spreading properties of the solder and its soldered joint have not yet been reported. In this study, physical, mechanical, and spreading properties of Sn-3.83Ag-4.83Bi solder and its joint are tested and discussed under specific conditions. Further research work is under development.

2. Experimental Procedure

2.1 Solder Preparation

Ingots of 99.95 wt.% Sn, 99.95 wt.% Ag, and 99.95 wt.% Bi were melted in air in a 75% Al_20_3 crucible protected by a cover of molten mixed eutectic salt (KCl: LiCl = 1.3:1 wt.%) for 1 h at about 450 °C. Mechanical agitation was used to mix the compositions. After removing the protective cover, the molten solder was cast into a steel mold to form solder rod.

Solder block was pulverized under N_2 atmosphere. After sifting, −325 to ~500 mesh powder was chosen for preparation of the solder paste. Meanwhile, the powder was sealed immediately after being sifted with vacuum sealer to avoid oxidation. Solder paste was obtained by uniformly mixing powder and RMA flux with the proportion of 1 flux, 8 powder (weight percentage).

2.2 Physical Property Testing

The cooling curve was investigated by measuring the temperature variation of molten solder in an Al_20_3 crucible. The solder was melted at 400 °C and then cooled at a cooling rate of 10°/min. A thermocouple for measuring the temperature changes was embedded in the bulk solder. The thermocouple had been calibrated with pure Sn to ensure the correct reading of the melting points.

The thermal behavior of the solder was also investigated with a differential scanning calorimeter (DSC). About 10 mg of solder powder (−200 mesh) was heated in a Al_20_3 cell at a heating rate of 10°/min up to 300 °C under N_2 atmosphere. Only the heating curve was investigated.

Coefficiency of thermal expansion (CTE) was tested between 30° and 100 °C at a heating rate of 2°/min on a Formastor-Digital Automatic Strain Tester using the sample as shown in Fig. 1. The specimen was heat-treated for 1 h at 100 °C before testing.

Electrical resistance was measured at 298 K. The specimen was belt rolled with the size of 2 × 0.1 × 100 mm. Electrical conductivity was obtained from the reciprocal of electrical resistance of the solder. Then electrical conductivity was transformed to International Copper Association Standard (ICAS) value.

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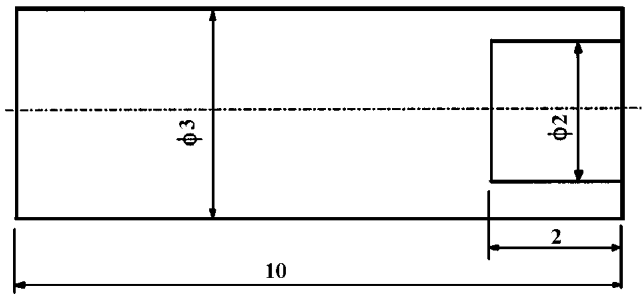

Fig. 1 Specimen for CTE test

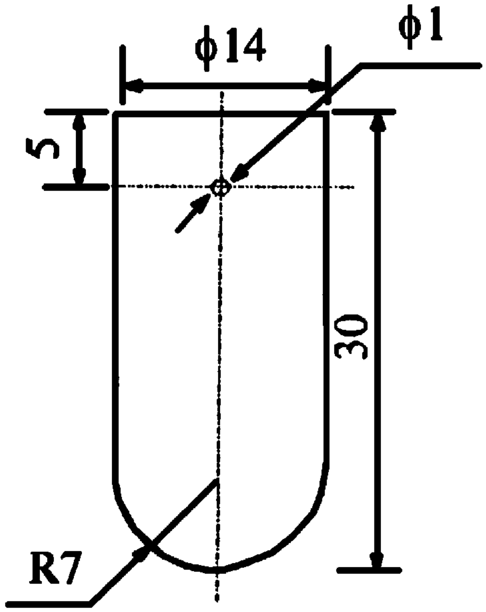

Fig. 2 Speciment for thermal conductivity test

Thermal conductivity of the solder was tested at 20°-100 °C according to the standard GJB1221.1-91. The specimen is shown in Fig. 2.

2.3 Solderability Measurement

Wetting and spreading behavior of the solder alloy was evaluated by a spreading experiment. Solder block (200 mg) was heated on copper substrate at 234 °C for 15 s, and the spreading area was measured. The copper had been precoated with RMA flux. Solder paste (233 mg) was put directly on the bare copper substrate. The heating procedure and testing method were the same as that of solder block. The result was compared with SnPb solder block.

2.4 Mechanical Property Measurement

The homogeneous molten solder was inhaled into a 5 mm diameter glass tube and then cooled in the air. The rod was then machined to tensile specimens as shown in Fig. 3. All specimens were annealed at 100 °C for 1 h before the test. Tensile tests were carried out on an Instron testing machine at a strain rate of 10^{-2} at 298 K to obtain data on tensile strength, yielding strength, fracture elongation, and energy. Soldered lap joint was obtained at 234 °C for 5 min in a furnace. The substrate was copper precoated with RMA flux. Solder block was sandwiched between the base metal. Copper wire (0.1 mm) was used to control the distance of the joint. The specimen is shown in Fig. 4.

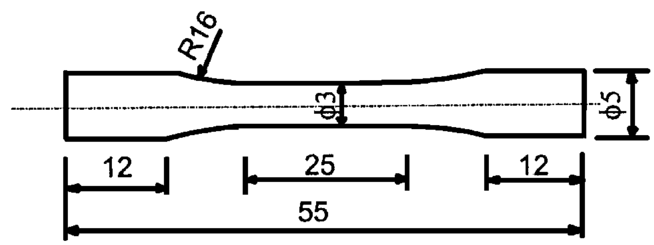

Fig. 3 Specimen for tensile test

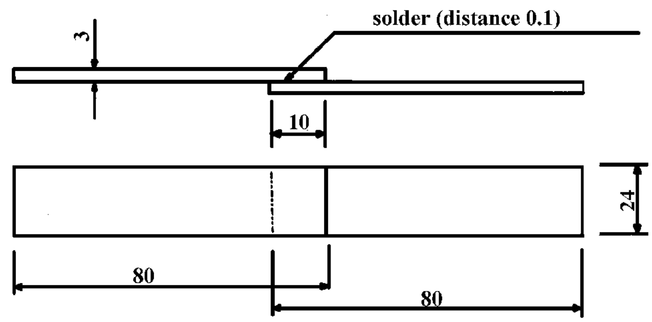

Fig. 4 Specimen for joint strength test

2.5 Fracture Appearance and Microstructure Analysis

The fracture appearance of the tensile specimen of the bulk solder was analyzed with SEM; microstructure and phase (especially IMC phase) of the as-cast solder were analyzed with the optical microscope and EDAX.

For comparison, data on the SnPb solder were listed either by testing or by extracting from relevant references as noted.

3. Result and Discussion

3.1 Physical Properties

A plateau region existed at 212 °C in the cooling curve of this solder as seen in Fig. 5. No inflection temperature other than 212 °C was observed in the cooling curve, indicating that the composition was very close to the eutectic composition as designed. DSC curve (Fig. 6) showed only one peak upon heating, meaning the onset melting point was 210.5 °C, which was very close to the result of the cooling curve. It was evident that the solder in this article was probably eutectic composition.

Table 1 lists the CTE tested data. CTE of this lead-free solder was lower than that of SnPb solder. It was between the CTE of the two substrates, which was beneficial to balance the thermal mismatch of the substrates. Therefore, during the cool-

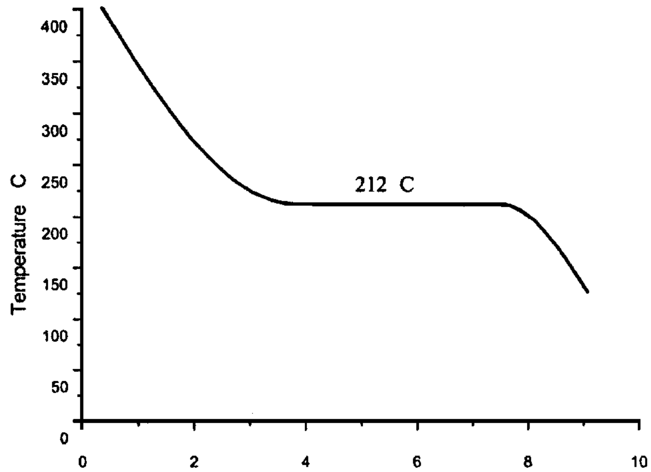

Fig. 5 Cooling curve of Sn-3.33Ag-4.83Bi solder

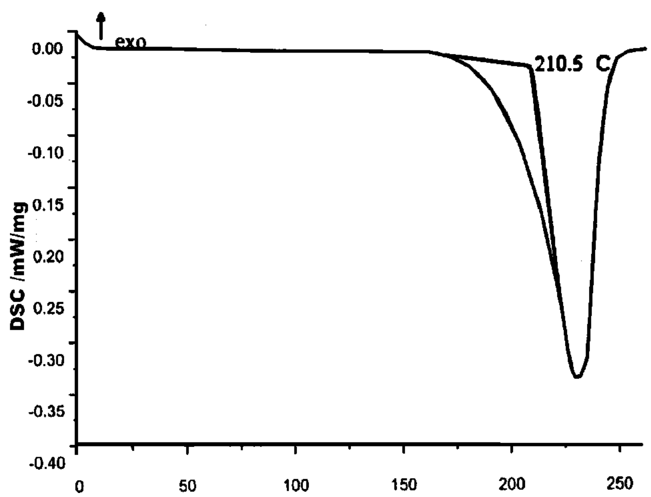

Fig. 6 DSC of Sn-3.33Ag-4.83Bi solder

ing period, the solder could absorb the thermal mismatch between the substrates, leading to the lower residual stress.

Electrical conductivity of SnAgBi solder and SnPb solder are shown in Table 2. Electrical conductivity of SnAgBi solder was $6.90 \times 10^{-6} \cdot \Omega^{-1} \cdot m^{-1}$, which was higher than that of SnPb solder, indicating that the developed lead-free solder was more beneficial than SnPb solder to conduct electricity and to prevent overheating produced in the circuit.

Thermal conductivity in Table 3 also indicates that SnAgBi solder was a good thermal conductor at working temperature. Therefore, the solder could hold and transfer the heat produced from electronic components. This was beneficial to lowering the temperature increase and to improving reliability during service.

3.2 Solderability

The spreading (wetting) behavior is very important to evaluate the weldability (processing). Because of the quick development and wide application of SMD in electronic industry, solder paste is widely used in the reflowing procedure. Meanwhile, there is a distinctive difference between the property of the bulk and powder condition of the solder. Simulating the actual reflowing procedures, with RMA flux, the solder block and solder paste have been tested under the same conditions. The results are shown in Table 4.

As temperature rises, solder block and paste began to melt and spread aided by RMA flux. But solder block spread with difficulty, with small spreading area, big reinforcement, and irregular form as seen in Fig. 7(a), whereas solder paste spread quickly, with large spreading area, lower reinforcement, and nearly regular sound circle form (Fig. 7b). Meanwhile, the spreading area of the solder paste was much larger than that of the SnPb solder block (Fig. 7c). Therefore, the solder completely met the demand of the electronic products to replace SnPb solder.

Table 1 Coefficiency of Thermal Expansion of the Solder and the Substrate

Material	SnAgBi Solder	Copper Substrate (a)	Circuit Board for SMD-1 (a)	Circuit Board for SMD-2 Al_2O_3 Ceramic (a)	SnPb Solder (b)
α ($\times 10^{-6} \cdot °C^{-1}$)	15.7	16.5	12	6.7	21.2

(a) Notes from Ref. 9.
(b) Notes from Ref. 10.

Table 2 Electrical Conductivity of the Solder

	SnAgBi	SnPb (a)
Electrical conductivity ($\times 10^{-6} \cdot \Omega^{-1} \cdot m^{-1}$)	6.90	6.63
ICAS (%)	12.3	11.8

(a) Note from Ref. 10.

Table 3 Thermal Conductivity of the Solder

Solder	Temperature (°C)	Thermal Diffusion Rate ($\times 10^{-5} \cdot m^2 \cdot s^{-1}$)	Thermal Conductivity ($W \cdot (m \cdot K)^{-1}$)
SnAgBi	20	3.42	55.2
	50	3.26	52.2
	100	3.09	50.6
SnPb (a)	20	—	50.9

(a) Note from Ref. 10.

Table 4 Spreading Area on Copper Substrate at 234 °C for 15 s

Solder	SnAgBi Solder Block	SnAgBi Solder Paste	SnPb Solder Block
Spreading area (mm^2)	43.89	230	74.4

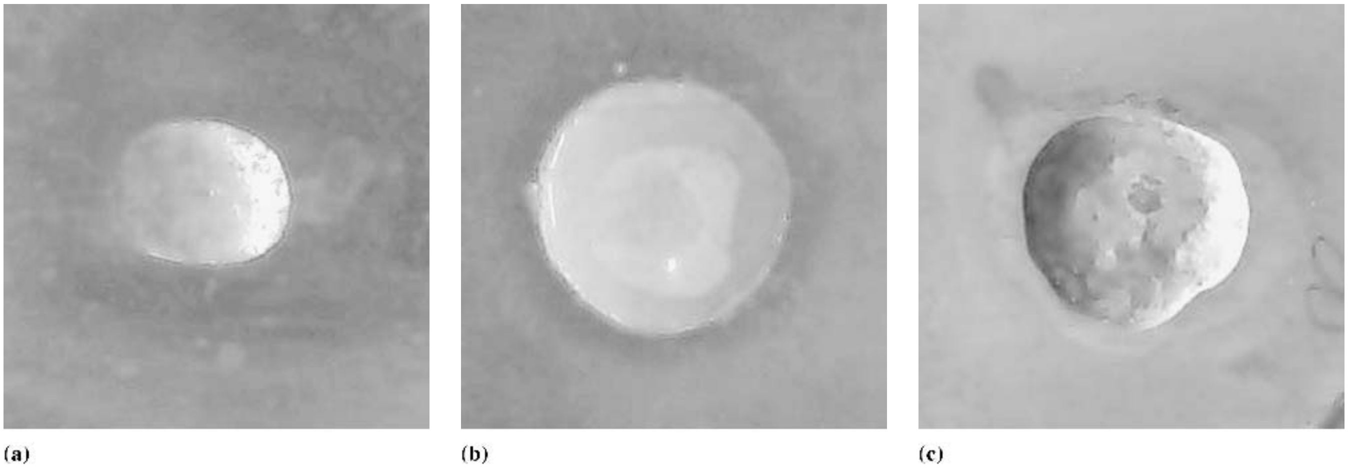

Fig. 7 Appearance of the spreading surface of solder on copper: (a) SnAgBi Solder block; (b) SnAgBi Solder paste; (c) SnPb solder block

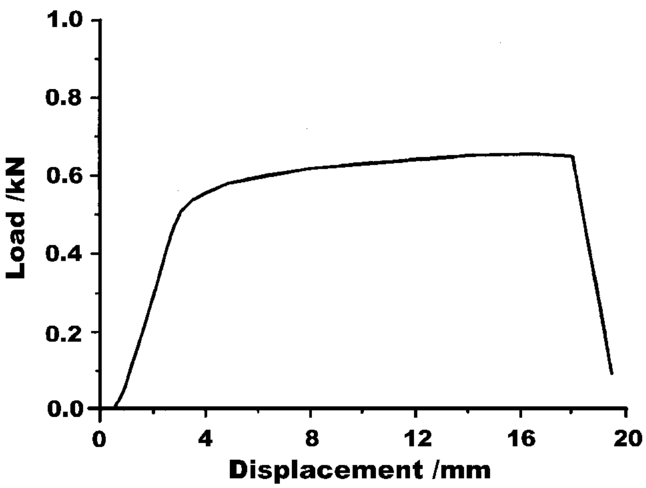

Fig. 8 Tensile curve of Sn-3.33Ag-4.83Bi solder

Table 5 Tensile Result of SnAgBi Solder and SnPb Solder and Their Soldered Joint

Solder	Tensile Strength (MPa)	Yield Strength (MPa)	Elon-gation (%)	Fracture Energy (J)	Joint Strength (MPa)
Sn-3.33 Ag-4.83Bi	63.87	2.79	17.67	9.61	40.72
Sn-37Pb	45.49	2.58	25.10	7.94	30.50

3.3 Mechanical Property

Figure 8 shows the tensile curve of the bulk solder. Mechanical properties of the bulk solder and the strength of the joint are listed in Table 5. SnAgBi solder had higher tensile and yielding strength, and lower elongation than that of SnPb solder. Its fracture energy was higher, meaning that it was more resistant to fracture. The joint strength made with SnAgBi solder was higher than that made with SnPb solder, whereas they were all lower than the strength of bulk solder. Fracture faces of the joint showed some un-fusion zone in the joint.

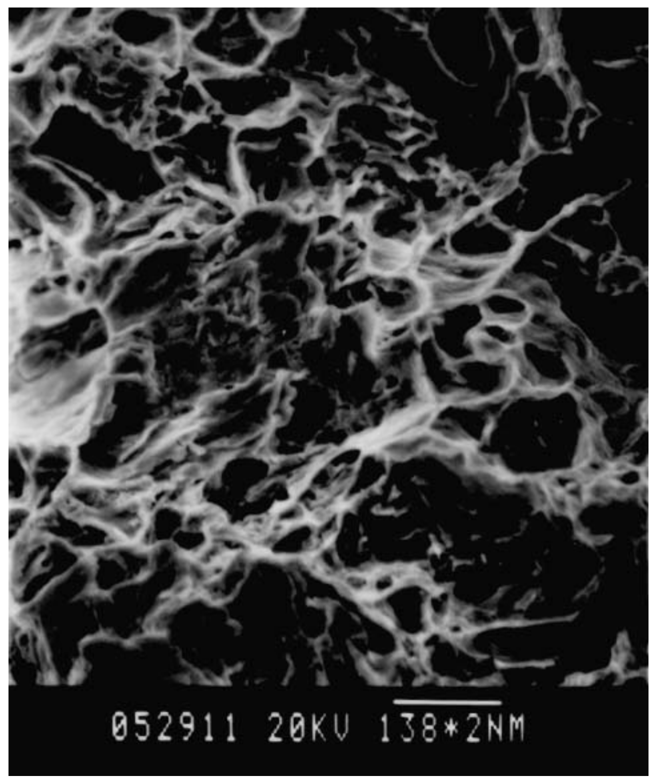

Fig. 9 Fracture appearance of the tensiled specimen of Sn-3.33Ag-4.83Bi solder

Figure 9 shows the fracture appearance of the tensile specimen. It was obviously characterized with tearing, plastic deformation, and dimples indicating a typical ductile failure appearance. Some brittle features in the surface showed a local less ductile appearance. As mentioned later, this might result from existence of brittle IMC.

Microstructure of the solder is shown in Fig. 10. It was composed of tin-based solid solution and many intermetallic compounds with various forms. The EDAX analysis result indicates that the irregular IMC was Ag_3Sn. Ag_3Sn can

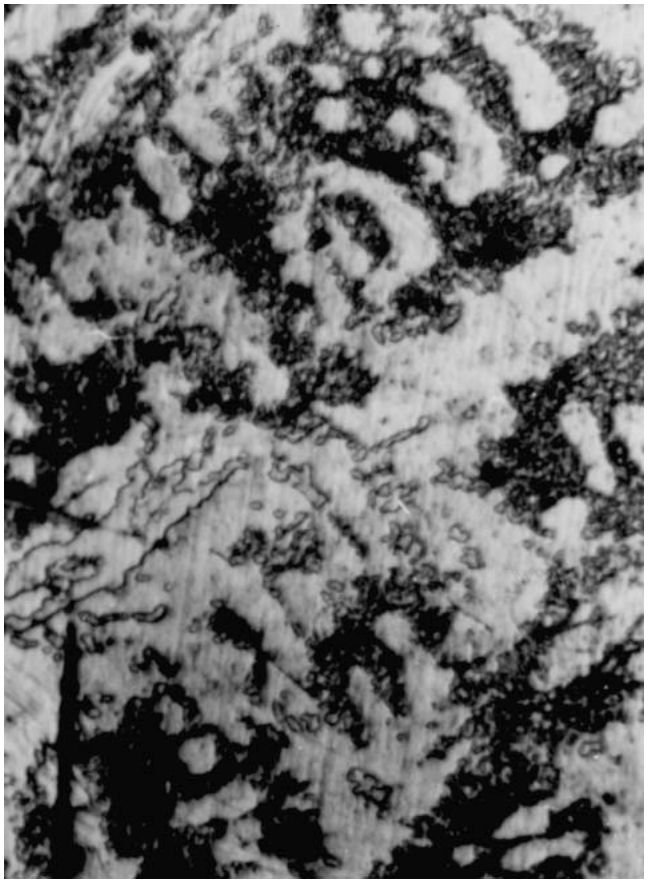

Fig. 10 Microstructure of Sn-3.33Ag-4.83Bi solder

strengthen the substrate. However, too-large-sized IMC would cut off the substrate and become a crack source to induce crack propagation when loaded. This behavior could decrease toughness of the substrate, as this test proved.

4. Conclusions

Sn-3.33Ag-4.83Bi alloy is close to ternary eutectic composition alloy. Melting point of the solder is about 210 °C-212 °C. Its coefficiency of thermal expansion (CTE) is 15.7×10^{-6}/°C, which is between that of PCBs and Cu substrates and is beneficial to decrease the mismatch of them. The solder is also a good electrical and thermal conductor.

SnAgBi solder paste has good solderability that can meet the demand of electronic products as a potential substitute for tin-lead solder.

The solder and its soldered joint have good mechanical property. Its fracture energy is higher than that of Sn-37Pb.

SnAgBi solder is made of tin-based solid solution and some intermetallic compound that can strengthen the substrate. These large blocks of IMC will cut the substrate, resulting in decreasing the toughness of the solder. SEM shows a mixture of ductile and brittle fracture mechanism.

Acknowledgments

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