

EFFECT OF AG NANOPOWDERS ON MICROSTRUCTURE, HARDNESS AND ELASTIC MODULUS OF SN-BI SOLDERS

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Abstract:

This paper presents the microstructure, hardness and elastic modulus of Sn58Bi, Sn57Bi1Ag and Ag nanopowders reinforced Sn58Bi composite solders. Microstructural observations reveal that the Ag nanopowders reinforced Sn58Bi composite solders have smaller grains of Ag3Sn and a more uniform Ag3Sn distribution in comparison with those of Sn57Bi1Ag solder. Nanoindentation test results show that the addition of Ag nanopowders has greatly enhanced the mechanical properties of Sn58Bi solder, i.e., it exhibits 13-30% increase in hardness and 10-22% increase in modulus of the composite solder. Besides, hardness and elastic modulus of solder are dependent on the size, distribution and the quantity of the second-phase.

1 Introduction

1.1 Manuscript preparation

Tin-lead solders have been extensively used in the electronic industry. However, the toxicity of lead combined with strict legislation to ban the use of lead-based solders have provided an inevitable driving force for the development of lead-free solder alloys. Recently, researchers have done large amounts of research into composition, mechanical properties and reliability of lead-free solders. Some achievements have partly met the urgent need of electronic industry. The miniaturization and multi-function of electronic products require that the solder joint shall withstand higher service temperature and severer thermo-mechanical fatigue and creep. The solder joint is required to have good ductility and good mechanical strength. An effective method is to develop lead-free composite solders.

Current research programmes / papers / experiments have focused on Sn-Cu, Sn-Ag, Sn-Zn and Sn-Ag-Cu alloy systems [1]. Undoubtedly, creep resistance and thermo fatigue resistance can be greatly improved by adding reinforcement particles including nano-sized or micro-sized metallic powder (e.g. Cu, Ag, Ni, Au, Al, Pt, Co, Zn, In, Sb, Ge, Mo, Ta) [2-11], intermetallic compound particle (e.g. Ni3Sn4, Cu6Sn5, Cu3Sn, Ag3Sn, TiNi) [12-14], metallic oxide powder (e.g. TiO2, Al2O3, ZrO2, Y2O3, Fe2O3, SnO2) [15-17], and other particles (e.g. SiC, CNT, POSS, TiB2) [18-22] into the conventional solder alloy.

At present, the existing literatures have studied the effect of certain reinforcement particle size on the microstructures, the mechanical properties and the interface structure of solder joints. However, the size effect on the mechanical properties of composite solder is still not clear. Furthermore, the

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difference between the molten solder alloy and the composite solder is not clear, either.

Among the lead-free solder candidates, Sn58Bi and Sn57Bi1Ag are considered to be ideal low melting point solders to replace Pb-containing solder alloys in surface mount microelectronic assembly interconnection. The low melting point Sn-Bi solder alloy has many advantages in special soldering applications, such as the solder joining at the temperature-sensitive zones in the outer layers of classification packaging. With the application of the low melting point solders, the influence of the soldering temperature on the inner layer of the classification packaging can be well reduced. In addition, Sn-58Bi solder is suitable for hermetic packaging of electronic devices and micro-electronic-mechanical systems (MEMS). However, the segregation of Bi and lower ductility limits the use of solder Sn-Bi. Composite solder can deal with this problem. Up to now, little research has been performed on Sn-Bi composite solder except by adding Y_2O_3 [23].

In this study, a novel method for producing the Sn58Bi composite solder reinforced with nano-Ag powder is introduced. The purpose of this work is to investigate the effect of three different sizes of Ag nano powders on the microstructures and the hardness of Sn-58Bi solder. For comparison, the microstructures and hardness of Sn58Bi and Sn57Bi1Ag solder have also been studied.

2 Experimental procedures

2.1 Material and sample preparation

The commercial Sn58Bi powder (size 25-45 μ m), Sn57Bi1Ag powder (size 25-45 μ m) and nano-scale Ag powders (the average sizes were 20nm, 50nm, 100nm, respectively) were purchased from the commercial vendors. The commercial flux paste was acquired from Yik Shing Tat Industrial Co., (China). The composite solder pastes were prepared with the following sequences:

- The Sn58Bi solder powders, Ag nanopowders and flux paste were pre-weighed, respectively.
- Ag nanopowders were dispersed into the solvent by supersonic to reduce the brittle agglomerations in the solder matrix.
- Then Ag nanopowders and flux paste were stirred in a ceramic crucible to ensure a homogeneous Ag nanopowder distribution in the composite flux paste.

d) The Sn58Bi powders and the composite flux paste were then stirred uniformly to prepare the composite solder paste. With three different sizes of Ag nanopowders, the prepared composite solder pastes were Sn58Bi-1wt. %Ag(20nm), Sn58Bi-1wt.%Ag(50nm), and Sn58Bi-1wt.%Ag(100nm). They were named as SB-Ag₂₀, SB-Ag₅₀, and SB-Ag₁₀₀, respectively in the following.

Sn58Bi solder paste and Sn57Bi1Ag solder paste were prepared respectively by mixing the solder powders and the flux paste uniformly. They were abbreviated as SB and SBA in the following.

A schematic of the experimental device was shown in Fig. 1. The samples were prepared with the following steps.

- The aluminum plate was preheated to 180 $^{\circ}$ C in the air.
- A certain amount of solder paste was put on the alumina ceramic plate which was on the top of the aluminum plate.
- The solder paste was heated by the hot aluminum plate for 1 minute. Then the solder paste was melted completely and a spherical ball with diameter of about 760 μ m was formed under the effect of the surface tension.
- The alumina ceramic plate was taken out from the heating chamber and the molten spherical ball was allowed to cool down to room temperature in air.
- The solidified solder ball was then removed from the alumina ceramic plate and cleaned by immersing into the acetone solution to remove the flux and the surface contaminates.

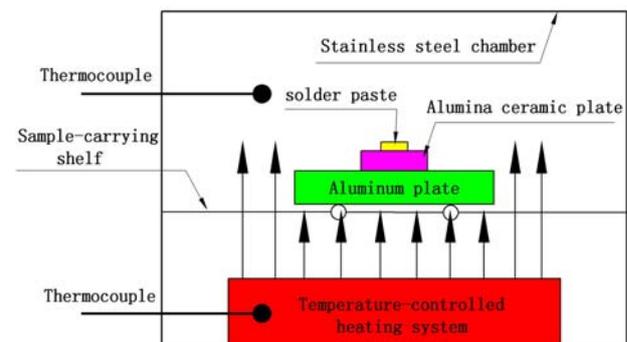


Figure 1. A schematic of the experimental device.

2.2 Microstructure characterization

The solidified solder balls were mounted in the epoxy for grinding. The standard metallographic procedures were performed to prepare the cross-section samples. The microstructures were identified using FE- S-4700 SEM equipped with energy-dispersive X-ray analysis (EDS). The SEM images in BSE mode were achieved.

2.3 Nanoindentation test

The hardness and the elastic modulus of the solder samples were obtained by nanoindentation tests with an NHT Nanoindenter (CSM co., Switzerland) which was equipped with a Berkovich diamond indenter. The resolutions of the loading and displacement systems are $0.04\mu\text{N}$ and 0.3nm , respectively. All the nanoindentation tests were conducted at room temperature. The indentation mode was load controlled and the loading rate was 10mN/s . The load of 100mN was selected. When the indentation load approached the peak value, the indentation process would hold 180s and then unload with an unloading rate of 50mN/s .

3 Results and discussion

Fig. 2 showed the typical eutectic microstructure of the Sn-58Bi solders in the as-soldered condition. The phases in the light regions were the bismuth-rich phases, while those in the dark regions represented the tin-rich phases.

The microstructures of the as-soldered Sn57Bi1Ag eutectic solders were shown in Fig. 3. The second-phase particles had the polygon granular morphology with the size of $1 \sim 3\mu\text{m}$, and they were confirmed to be Ag_3Sn by EDS analysis. The Bismuth-rich phase had the refining tendency due to the existence of Ag_3Sn .

Compared with those in the solder of Sn58Bi and Sn57Bi1Ag, much finer microstructures were observed in the as-soldered composite solders, as shown in Fig. 4. The uniform dispersion of finer Ag_3Sn in the composite solder hinders segregation of Bi effectively. The morphology of Ag_3Sn changed from the polygon granular shape to the short rod-like shape. The average size of Ag_3Sn was decreased below 50nm . The size of Ag_3Sn increased with the increase of Ag nanopowder size, and the morphology towards Sn57Bi1Ag.

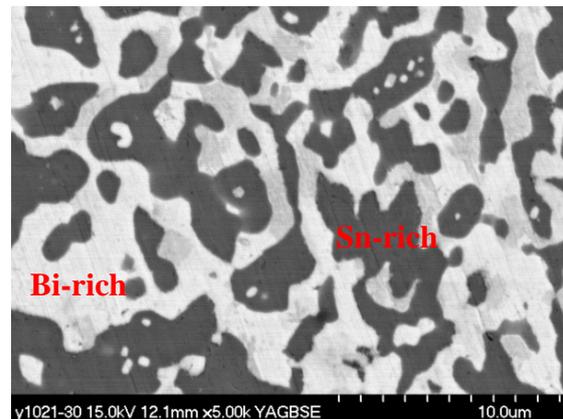


Figure 2. The microstructure of Sn58Bi.

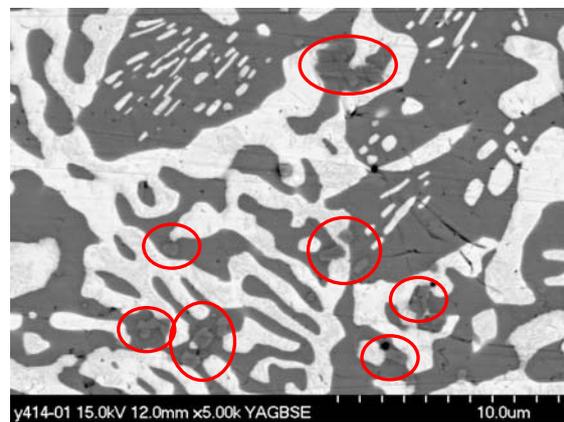
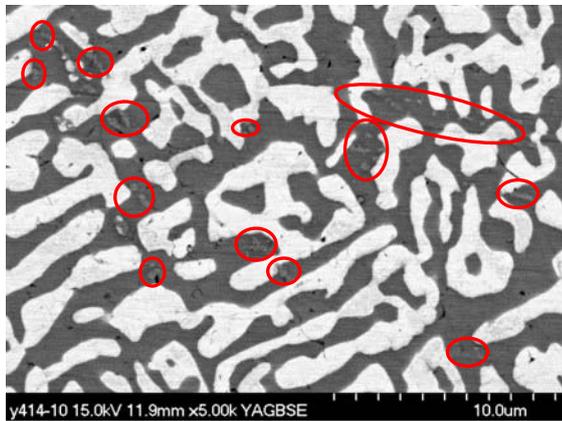


Figure 3. The microstructure of Sn57Bi1Ag.

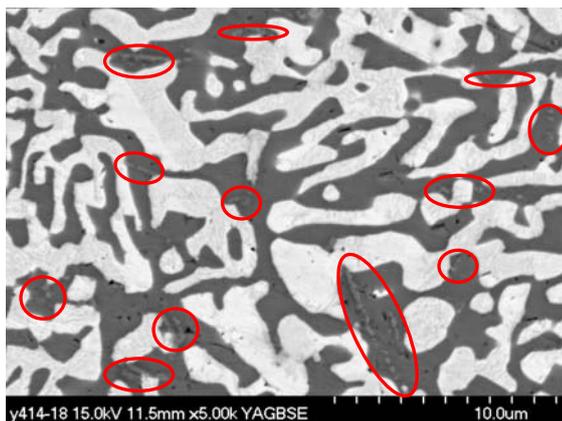
Typical morphology of residual indent in solder alloy is shown in Fig. 5. The side of an indent is about $35\mu\text{m}$. The microstructure under indent included tin-rich phase and bismuth-rich phase. So, indentation tests ensure the global mechanical response.

The hardness and the elastic modulus obtained from nanoindentation tests were summarized in Fig. 6 and Fig. 7. Results showed an increase in hardness of the composite solder from 13-30% and an increase in modulus from 10-22% in comparison with Sn58Bi solder. The enhancement of the hardness and modulus of a composite solder conform to the theory of dispersion strengthening. Furthermore, we found an interesting phenomenon between the composite solder and Sn57Bi1Ag solder. SB- Ag_{20} and Sn57Bi1Ag have a similar elastic modulus, but SB- Ag_{20} increases in hardness up to 13%. However, SB- Ag_{100} and Sn57Bi1Ag have similar hardness, while SB- Ag_{100} has an 8.3% decrease in elastic modulus.

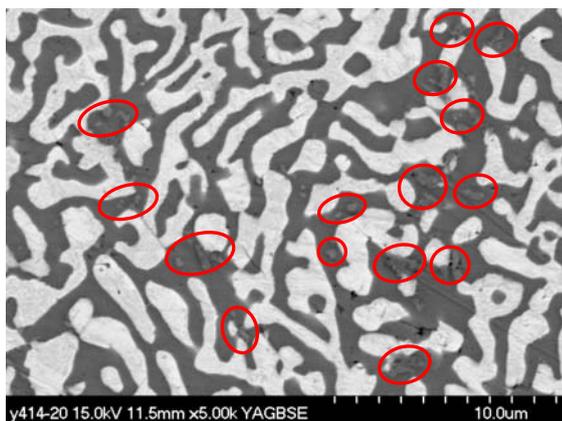
The reasons for this phenomenon were that finer grain structures of Ag_3Sn phases were well distributed in the composite solder alloy.



SB-Ag₂₀



SB-Ag₅₀



SB-Ag₁₀₀

Figure 4. The microstructure of composite solder.

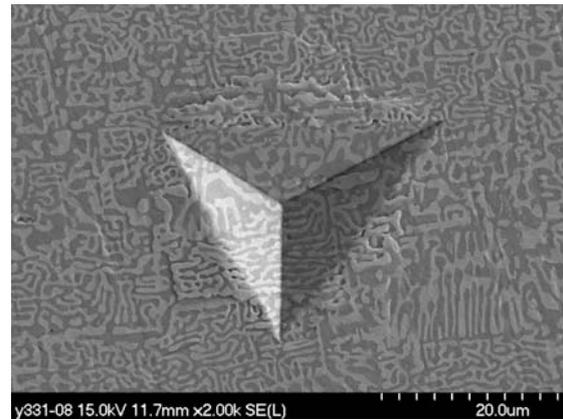


Figure 5. SEM image of residual indent on solder alloy.

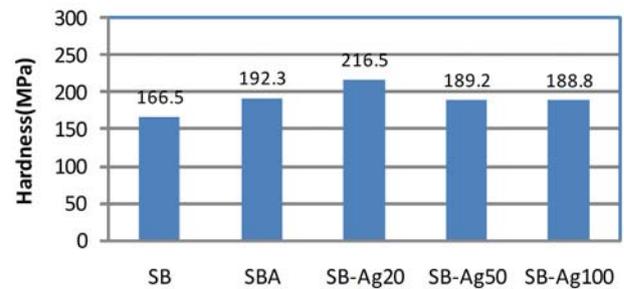


Figure 6. Hardness of solder alloys.

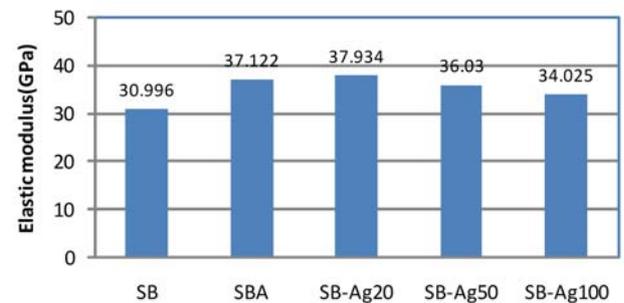


Figure 7. Elastic modulus of solder alloys.

During the compression deformation process, the nano scale second-phases (Ag_3Sn) would hinder the dislocation caused by the deformation and consequently the dislocation would pile up around the second-phases. When the dislocation pile-up was too large to be hindered by the second-phases, the dislocations would bypass the second-phases and kept moving, which meant that the temporarily suspending deformation would restart. That was the reason why different solders with similar elastic modulus exhibited different hardness. With an increase of Ag nanopowder size, the hardness and elastic modulus of the composite solder decreased

due to an increase of Ag_3Sn size. When the sizes of Ag nanopowders were 50nm and 100nm, the hardness of the corresponding composite solders was equal to that of SBA alloy. However, their elastic modulus was lower than the one of SBA solder. The composite solders exhibited better comprehensive mechanical properties, which were supposed to be dependent on the size, distribution and the quantity of Ag_3Sn .

4 Conclusion

The addition of Ag nanopowders with different sizes has greatly enhanced the comprehensive mechanical properties of Sn58Bi solder.

The composite solder prepared in this study had fine and more uniformly distributed Ag_3Sn compared with that in SBA solder.

The hardness and the elastic modulus of the solder were dependent on the size and the quantity of the second-phase.

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