# Microstructures Evolution and Its Influence on Mechanical Properties in Sn-Ag-Cu-Bi Lead-free Solders After Aging Treatment*

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**Abstract**: The current work investigated the influence of aging time on microstructures and mechanical properties in Sn-3Ag-0.5Cu, Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi solders. The effect of Bi was discussed based on the experimental results. The experimental results indicated that: the addition of Bi increased the tensile strength of the solders but decreased their elongation. After aging at different temperatures, Bi precipitated in Sn matrix in Bi-bearing solders, while the Bi-bearing solders exhibited stable mechanical properties. This can be attributed to the strengthening effect of Bi from solid solution strengthening to precipitating strengthening in the solders.

**Key words**: Pb-free solder; microstructure; aging; tensile properties
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## 1 Introduction

As the restriction of lead use in industrial fields has been strongly promoted because of the environmental protection on water resources, the development of lead-free is becoming a critical subject for the new generations in electronics and automobile products[1]. As a matter of fact, there have been many works reported on new solders in the last decade. Among them, Sn-Ag-Cu-Bi is regarded as one with high quality and performance and can meet the requirement electronic packaging. Researches have been reported on their fatigue property and joint performances[2-3].

Normally, solders in joints are already worked at high homologous temperature even at room temperature because of their low melting temperatures. Therefore, the microstructures are unstable during applications. Room temperature aging has been reported to reduce the shear strength of a 63Sn-37Pb solder by about 10%[4] and that of 60Sn-40Pb solder by nearly 30%[5]. Effect of aging time on interfacial microstructure and growth of intermetallic compounds (IMC) was performed in Sn-3.5Ag and Sn-Bi solder joints[6,7]. It was indicated that the morphology of IMCs and precipitates of Bismuth occurred in supersaturated Sn matrix changed during aging[7,8]. It is believed that the microstructure evolution can significantly influence the reliability of solder joints, therefore the knowledge of microstructure change in solders as well as in joints is important. The understandings of the effect of microstructure change on mechanical properties are required. Although there are a lot of reports on microstructure evolution during aging in Sn-Bi, Sn-Ag-Bi and Sn-Pb solders, no report has been found in Sn-Ag-Cu-Bi solder and the investigation about the effect of Bi in the solders.

The current work investigated the influence of aging time on microstructures and mechanical properties in Sn-3Ag-0.5Cu, Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi solders. The effect of Bi was discussed based on the experimental results.

## 2 Experiments

Three lead free solder alloys, Sn-3Ag-0.5Cu, Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi, were used in experiments. They were re-melted and cast into bars with diameter of 8 mm in a copper mould. Compositions as well as the values of solidus and liquidus of these solders are listed in Tab.1. It is found that the value of solidus temperature decreases with increasing Bi content, while the liquidus temperature is not sensitive to Bi content.

The solder bars were machined to dog-bar tensile specimens with a diameter of 5 mm and gauge length of 20 mm. The samples for microstructure observation were also cut from the bars. The tensile specimens and microstructural samples were then aged in the ovens maintained at constant temperatures of 120 ℃, 150 ℃ and 170 ℃ for 100 hours. After aging treatment, the surfaces of the tensile specimens were fine polished. The tensile tests were performed at strain rate of 0.004 $s^{-1}$ by using CCS testing system.

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The microstructures of all the samples were observed by using optical microscopy and scanning electronic microscopy. Energy dispersive X-ray spectroscopy (EDS) was used to distinguish among different phases in the solders. For the microstructural observations, the samples were polished down to 0.3 μm alumina powder, then etched using a solution containing 5 mL HCl, 2 g $FeCl_3$, 30 mL distilled water and 60 mL alcohol.

## 3 Results and discussion

### 3.1 Microstructure evolution

The micrographs of the solders right after solidification (before aging treatment) are shown in Fig. 1. It is found that the microstructures of all the solders are composed of island-like Sn-rich phase and Sn-Ag-Cu eutectics. The eutectics are supposed to be a mixture of Cu6Sn5 and Ag3Sn intermetallics in Sn-rich matrix by X-ray examination, which also follows the binary Sn-Ag and Sn-Cu diagrams. The island-like Sn-rich phase is the pro-eutectic phase with dendritic features. The size of the Sn-rich phase decreased with the addition of Bi. The microstructure does not significantly change with the addition of Bi as the Sn-rich phase can dissolve substantial amount of Bi[9].

**Tab. 1 Chemical compositions of the materials used**

| materials | Chemical composition/% | | | | θ(liquidus)/℃ | θ(solidus)/℃ |
|---|---|---|---|---|---|---|
| | Sn | Ag | Cu | Bi | | |
| SnAgCu | 96.5 | 3 | 0.5 | 0 | 219 | 217 |
| SnAgCuBi1 | 95.5 | 3 | 0.5 | 1 | 219.5 | 213 |
| SnAgCuBi3 | 93.5 | 3 | 0.5 | 3 | 219.5 | 207 |

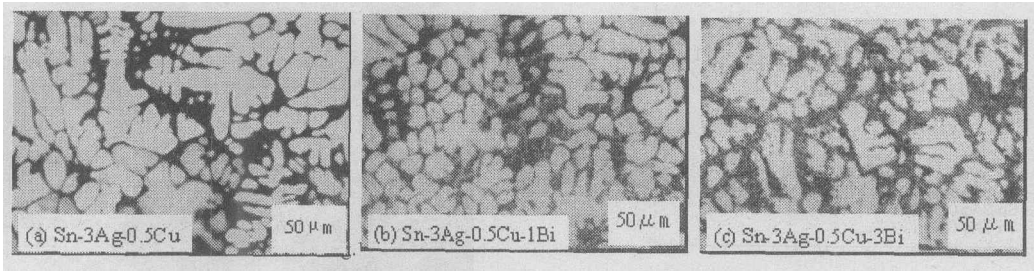


**Fig. 1 Microstructures of the alloys used**

After aging treatment, coarsening of the intermetallics compounds can be observed in all the three solders as can be seen in Fig. 2. The higher the aging temperature, the coarser the intermetallics compounds. By analyzing the elemental compositions of the particles using EDX, it seems that the larger particles tend to be Cu6Sn5 while the smaller tend to be Ag3Sn. However, no precipitation of Bi – rich particles was observed either in Sn-3Ag-0.5Cu or in Sn-3Ag-0.5Cu-1Bi solder under all the aging conditions. It is reasonable as the solid solubility limit of Bi in Sn at room temperature is about 1% from binary Sn-Bi phase diagram. It is therefore supposed that in the solders with Bi amount less than 1%, the microstructure composed of Sn-rich phase and Sn-Ag-Cu eutectics, and only the intermetallics coarsened during aging treatment. For the Sn-3Ag-0.5Cu-3Bi solder, fine precipitates were observed within Sn-rich phase in a Sn-3Ag-0.5Cu-3Bi specimen after aged at 120 ℃ for 100 h as shown in Fig. 3, which was determined as Bi-rich phase by using EDX.

The precipitation was not found either in as-cast specimen or in the specimens after aged at 150 ℃ and

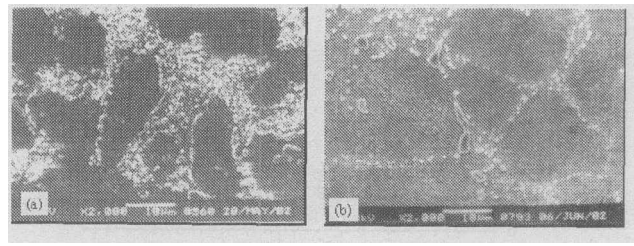

**Fig. 2 Microstructures of Sn-3Ag-0.5Cu-1Bi alloy after aging treatment**
**(a)** 120 ℃, 100 **h**; **(b)** 170 ℃, 100 **h**

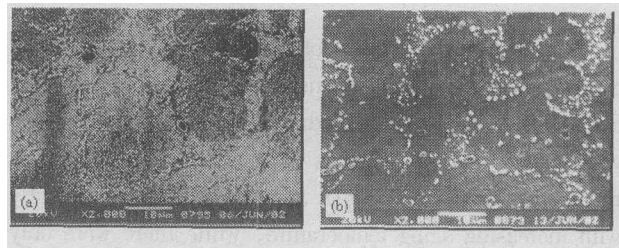

**Fig. 3 Microstructures of Sn-3Ag-0.5Cu-3Bi alloy after aging treatment**
**(a)** 120 ℃, 100 **h**; **(b)** 170 ℃, 100 **h**

170 ℃ for 100 h. It is therefore supposed that Bi supersaturated dissolved in Sn-rich phase in the as-cast specimen as well as those after aged at 150 and 170 ℃, while the solid solubility limit of Bi at 150 ℃ is below 3%.

### 3.2 Tensile test results

Fig.4(a) illustrates the relationship between tensile strength and aging temperatures for the solders experienced various aging temperatures. In point of Bi effect, it can be seen that the tensile strength increased with increasing Bi content for all the conditions. From the viewpoint of aging temperature, it is found that the tensile strength of Sn-3Ag-0.5Cu decreased significantly with increasing aging temperatures,, while there were only slight changes of the strength in Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi solders. Similar behavior was also observed in the relationship between hardness and aging temperatures for the solders as shown in Fig.4(b).

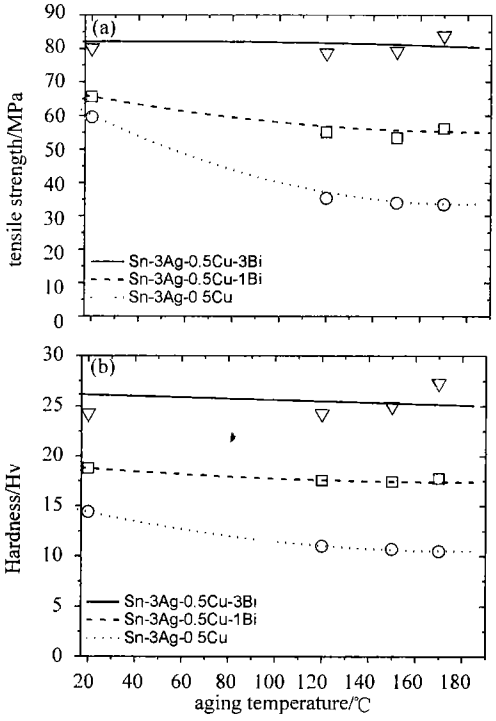


**Fig.4 The tensile strength and hardness of the alloys as a function of aging temperature**

Fig.5 plots the results of elongation of the solders as a function of aging temperature. It can be seen that the Sn-3Ag-0.5Cu-3Bi solder exhibited the lowest elongation while the Sn-3Ag-0.5Cu has the highest one. Moreover, the elongation of Sn-3Ag-0.5Cu decreased significantly with increasing aging temperature, while there were only slight changes of the strength in Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi solders. From the observation of fractographics, a ductile feature was dominant on the fracture surfaces as shown in Fig.6.

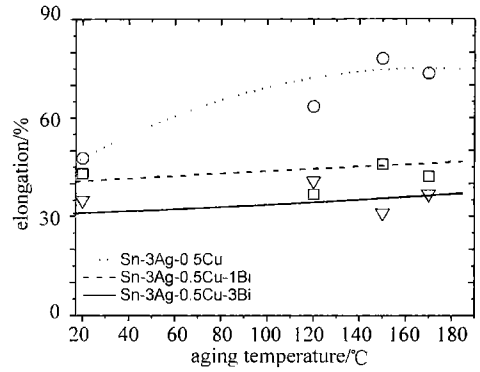


**Fig.5 The elongation of the alloys as a function of aging temperature**

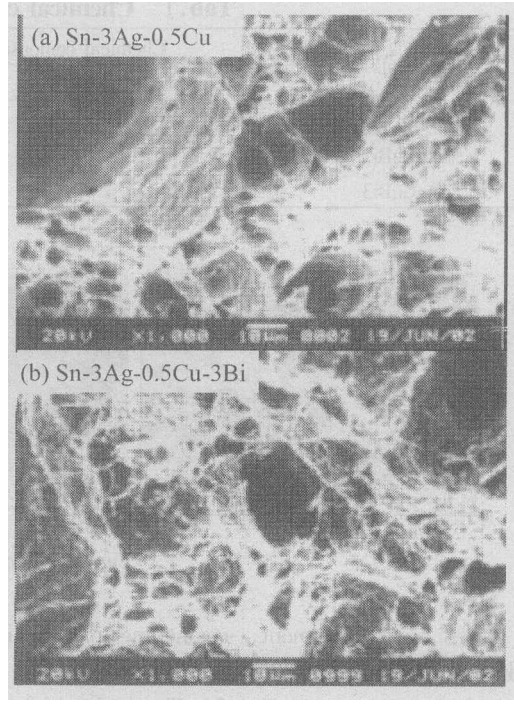


**Fig.6 Fractographics of the as-cast samples after tensile test**

### 3.3 Discussions

Sn-Ag-Cu solder is regarded as a candidate of Pb-bearing solder. It has superior mechanical properties to Sn-Pb solder. However, it is found from current research that the mechanical property, as well as microstructure, depended strongly on the aging temperature. The significant decrease of tensile strength is attributed to the coarsening of Cu6Sn5 and Ag3Sn intermetallics.

The Sn-Ag-Cu-Bi solders have higher tensile strength by comparison to Sn-Ag-Cu solder. However, it has been demonstrated that the addition of Bi above a certain concentration is harmful to the elongation[10,11]. From current results, it is interesting to note that the strength, hardness and elongation kept relative stable values with aging temperature in Sn-Ag-Cu-Bi solders as shown in Fig.4 and Fig.5. As the intermetallics coarsening was

also occurred in the Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi solders after aging treatment as can be seen in Fig.2 and 3. It is assumed that the stable characteristics of mechanical properties resulted from the strengthening effect of Bi.

Bi is often used in solders to reduce the melting temperature. From Sn-Bi binary equilibrium phase diagram, Bi has about 1% of solubility at room temperature, while it has significant solubility at high temperature (i.e.: 21% at 158 ℃ and about 11% at 120 ℃). However, it was found that Bi precipitated in Sn-3Ag-0.5Cu-3Bi solder after aged at 120 ℃. This phenomenon implies that the solid solubility of Bi in Sn decreases substantially with the addition of Ag and Cu. From the obtained limit data, it is supposed that the solid solubility limit of Bi in Sn at 120 ℃ is about 1% ~ 2%, while that at 170 ℃ is estimated to be about 3% ~ 5%. As Bi normally dissolved in Sn matrix in the current solders, the significant increase of strengths in Sn-Ag-Cu-bi solders is contributed to the solid strengthening factor.

If Bi precipitated from Sn matrix, it may produce an expansion and cause strain hardening to accommodate the expansion[12], and then exhibited obvious precipitate strengthening effect. It is therefore assumed that the stable mechanical properties of Bi-bearing solders may attribute to the strengthening effect of Bi from solid solution strengthening to precipitating strengthening in the solders.

## 4 Conclusions

This paper investigated the effect of Bi on microstructures and mechanical properties in Sn-3Ag-0.5Cu, Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi Pb-free solders. It is concluded that:

(1) The addition of Bi increased the tensile strength but decreased their elongation in Sn-3Ag-0.5Cu solders.

(2) After aging at different temperatures, the tensile strength of the Sn-3Ag-0.5Cu solder decreased dramatically with increasing aging temperature, while the elongation of the solder increased notably, however, no obvious change in the tensile strength and elongation of Sn-3Ag-0.5Cu-1Bi and Sn-3Ag-0.5Cu-3Bi was observed after aging treatments.

(3) From microstructure examination, it was seen from Sn-3Ag-0.5Cu-3Bi that Bi precipitated in Sn-matrix after aged at 120 ℃, which was not found for other samples. It is therefore assumed that the stable mechanical properties of Bi-bearing solders may attribute to the strengthening effect of Bi from solid solution strengthening to precipitating strengthening in the solders.

**References:**


[1] Jin S. Developing lead-free solder challenge and opportunity [J]. *JOM*, 1993(7):13.

[2] Zhao J, Mutoh Y, Miyashita Y, et al. Fatigue crack growth behavior of Sn-Ag-Cu and Sn-Ag-Cu-Bi lead-free solders[J]. *J Electronic Materials*, 2002,31(8): 879 - 886.

[3] Mutoh Y, Zhao J, Miyashita Y, et al. *Soldering & Surface Mount Technology*, 2002,14(3):37 - 45.

[4] Lampe B T, Welding J. *Research Supplement*, 1976, 55: 330s - 340s.

[5] Whitemore M A, Harris P G, Chaggar K S, et al. Presented at NEPCON Europe, Middlesex, U. K., 1990.

[6] Choi W K, Lee H M. *J Electronic Materials*, 2000,29(10): 1207 - 1213.

[7] Chen C, Ho C E, Lin A H, et al. *J Electronic Materials*, 2000,29(10): 1200 - 1206.

[8] Miao H W, Duh J G. *Chemistry and Physics*, 2001, 71: 255 - 271.

[9] Frear D R. The mechanical behavior of interconnect materials for electronic packaging[J]. *JOM*, 1996,48:49 - 53.

[10] Vianco P T, Rejent J A. Properties of ternary Sn-Ag-Bi solder alloys[J]. *J Electronic Materials*, 1999, 28(10): 1138 - 43.

[11] Kariya Y, Otsuka M. *J Electronic Materials*, 1998,27(7): 866 - 870.

[12] Glazer J. *International Materials Reviews*, 1995,40(2): 65 - 93.


# 时效处理对 Sn-Ag-Cu-Bi 无铅钎料显微组织和力学性能的影响


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**摘 要:** 主要研究了时效处理对 Sn-3Ag-0.5Cu、Sn-3Ag-0.5Cu-1Bi、Sn-3Ag-0.5Cu-3Bi 无铅钎料显微组织和力学性能的影响,并根据试验结果讨论了 Bi 元素的作用。试验结果表明:Bi 的加入提高了钎料的抗拉强度,但降低了其延伸率。通过在不同温度下时效处理,在含 Bi 的钎料中,Bi 在 Sn 基体中析出,而含 Bi 的钎料表现出相对稳定的力学性能。这可归因于 Bi 的固溶强化与弥散强化作用的转化。



**关键词:** 无铅钎料; 微观组织; 时效; 拉伸性能

**中图分类号:** TG42 **文献标识码:** A