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| Citation     | Transactions of JWRI. 2012, 41(2), p. 51-54                                                          |
| Version Type | VoR                                                                                                  |
| URL          | <a href="https://doi.org/10.18910/24863">https://doi.org/10.18910/24863</a>                          |
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# Effects of Ag Content on the Mechanical Properties of Bi-Ag Alloys Substitutable for Pb based Solder

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## Abstract

*As one of the candidate materials for the high-temperature-resistant joining materials which substitute from the conventional Pb-rich solder, Bi-Ag solder alloys were used to investigate the characteristics. The mechanical properties have been investigated on lead-free Bi-Ag alloys using tensile tests to clarify the important characteristics for solder alloys having reflow resistant relatively high melting temperature solders. The tensile strength gradually increased with increase of Ag content, however, the elongation showed a minimum at eutectic Bi-2.5Ag and it only slightly increased with increase of Ag content up to 11%Ag for quenched alloys. On the other hand, air cooled Bi-11Ag alloy showed improved elongation about 20%, the value is much higher than that of quenched one, about 3%. The hypereutectic Bi-11Ag solder can be used as a solder material having relatively good wettability and mechanical properties, in particular it showed elongation of 20% under air cooled condition.*

**KEY WORDS:** (Bi-Ag alloys), (Tensile strength), (Elongation), (Solidification rate), (Primary Ag phase)

## 1. Introduction

Recently, heat generation in electronic components and soldering tends to increase markedly in devices with high-density packaging. In particular, because electronic equipment for industrial and automotive applications, as represented by power devices, is used under severe environments characterized by large applied current, vibration, etc., the strength properties of Pb-free solders used for joining parts have a large effect on the durability and reliability of those parts. Here, as the joining materials of the electronic equipment, Sn-Ag-Cu lead free solders weren't applicable because they remelt in multi-reflow processes (process temperature is about 250 °C) as the melting point of Sn-Ag-Cu solders are about 220 °C. Moreover, mechanical properties of those solders deteriorate by Sn recrystallization and softening under the high temperature environment<sup>1)-3)</sup>.

Based on the above-mentioned background, a new alloy system, Bi-Ag solder alloys, has been considered as a replacement for high Pb solders in high-temperature applications<sup>4)-7)</sup>. One of the basic requirements for high-temperature Pb-free solder should be higher than 260°C; so that the solder is capable of surviving secondary reflow at 250°C, and the liquidus needs to be lower than

400 °C, due to the limitation of the heat-resistant temperature of the Si chip. Bi-Ag eutectic solder alloy exhibits an acceptable melting point (the eutectic temperature is 262°C at the eutectic composition, Bi-2.5 mass%Ag), similar hardness to that of Pb-5 mass%Sn, and affordable cost.

Song has investigated the tensile behavior of lead-free Bi-Ag solder alloys<sup>4),5)</sup>. They confirmed that Bi-Ag/Cu joints possessed tensile strength comparable to that of Pb-5 mass%Sn /Cu joints. However, the ductility of lead-free Bi-Ag solder alloys that are essential to the solder mount properties of the product, were not examined. Therefore, the fundamental solder mount properties, i.e., the mechanical properties, of Bi-Ag solder alloys were evaluated.

## 2. Experimental

### 2.1 Evaluation of the mechanical properties of bulk Bi-Ag solder alloys

Evaluations of the mechanical properties of bulk solder alloys were performed using the tensile test. The chemical compositions of the solder alloys and their melting ranges, i.e., The amount of liquid phase was calculated by using Bi-Ag binary phase diagram,

† Received on December 17, 2012

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

were shown in **Table 1**. The test specimens were prepared as follows. At first, the solder alloy was melted in an electric furnace heated to its melting temperature in an aluminum crucible. The temperature was higher than the liquidus temperature of each of the solder alloys by 100 °C (this method was based on the JIS Z 3198-2 standard). Next, the melted solder alloy was poured into a mold made of stainless steel to create a round bar with a diameter of 10 mm and length of 70 mm. Here, there were two methods for the casting, that is, air-cooling and rapid quenching.

In the case of air-cooling method, the molten solder alloys were cast in a heating jig at the same temperature as heating an aluminum crucible and then solidified by air-cooling. In the case of quenching method, the molten solder alloys were cast in a jig at room temperature and then solidified. Cast solder alloys were machined to dumbbell-shaped specimens (the parallel part had a diameter of 4 mm and length of 20 mm). The tensile strength and elongation of each solder alloy were measured under constant tensile speed of 0.24 mm/min, that is, the strain rate was  $2 \times 10^{-4}$  /s at room temperature by using an Instron type tensile test equipment.

### 2.2 Improvement in the ductility of bulk Bi-Ag solder alloys

The solidification rate was changed when casting the Bi-Ag solder alloys in order to change their microstructure. There were two kinds of specimens: quenched and air-cooled. The solidification rate of the quenched specimens was about 303 °C/s and that for the air-cooled specimens was about 0.5 °C/s. Here, the process temperature was higher by 100 °C than the liquidus temperature. In order to examine the microstructure, the specimens were prepared by wet grinding.

After polishing, microstructural analyses were performed using scanning electron microscopy (SEM, Hitachi SU-70). After tensile tests, the fracture surfaces were also observed using SEM. Moreover, in order to quantify the dispersion degree of primary Ag phase, both the size of primary Ag phase and the distance between adjacent primary Ag phase was measured based on SEM image.

**Table 1** Chemical compositions of solder alloys and their melting temperature ranges

| Symbol   | Bi (mass%) | Ag (mass%) | Solidus line(°C) | Liquidus Line(°C) | Amount of liquidus phase | Compositions   |
|----------|------------|------------|------------------|-------------------|--------------------------|----------------|
| Bi       | 100        | —          | 271              | 271               | 100                      | Pure Bi        |
| Bi-2.5Ag | Bal.       | 2.6        | 262              | 262               | 100                      | Eutectic       |
| Bi-7.0Ag | Bal.       | 7.0        | 262              | 338               | 97                       | Hyper-eutectic |
| Bi-11Ag  | Bal.       | 11.1       | 262              | 360               | 93                       | Hyper-eutectic |

### 3. Results

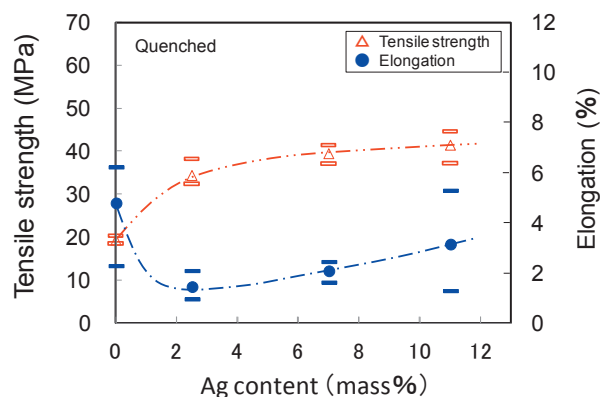
#### 3.1 Evaluation of the mechanical properties of bulk Bi-Ag solder alloys

**Figure 1** shows the result of the evaluation of the mechanical properties, i.e., the tensile strength and elongation, of quenched Bi-Ag solder alloys at room temperature. As the Ag content of the Bi-Ag solder alloys increased, the tensile strength increased and the average value was over 40 MPa for Bi-11Ag solder alloy. The elongation of Bi-2.5Ag solder alloy was the minimum and that of Bi-Ag solder alloys increased gradually as Ag content increased and the elongation became about 3 % when the Ag content was 11 mass%.

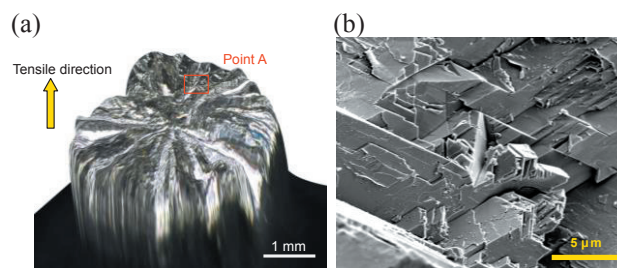
The reason that Bi-2.5Ag eutectic solder alloy showed the minimum elongation is not sufficiently clear, however, the appearance of soft Ag primary phase in hyper-eutectics solder alloys, Bi-7Ag and Bi-11Ag solder alloy, may be the one reason of slightly increased elongation in these solder alloys.

#### 3.2 Improvement in the ductility of bulk Bi-Ag solder alloys

**Figure 2** shows the fracture surface of the Bi-11Ag solder alloys after tensile test. As can be seen in **Fig. 2(b)**, the fracture surface of the Bi-11Ag solder alloys showed a typical brittle fracture whereas a conventional Sn rich lead-free solder would show ductility. In order to improve the ductility of the Bi-Ag solder alloys, the dependence of ductility on the solidification rate was investigated.



**Fig. 1** Changes of tensile strength and elongation of Bi-Ag solder alloys with Ag content.



**Fig. 2** Fracture surface of Bi-11Ag solder alloy. (a) perspective, (b) magnification of point A.

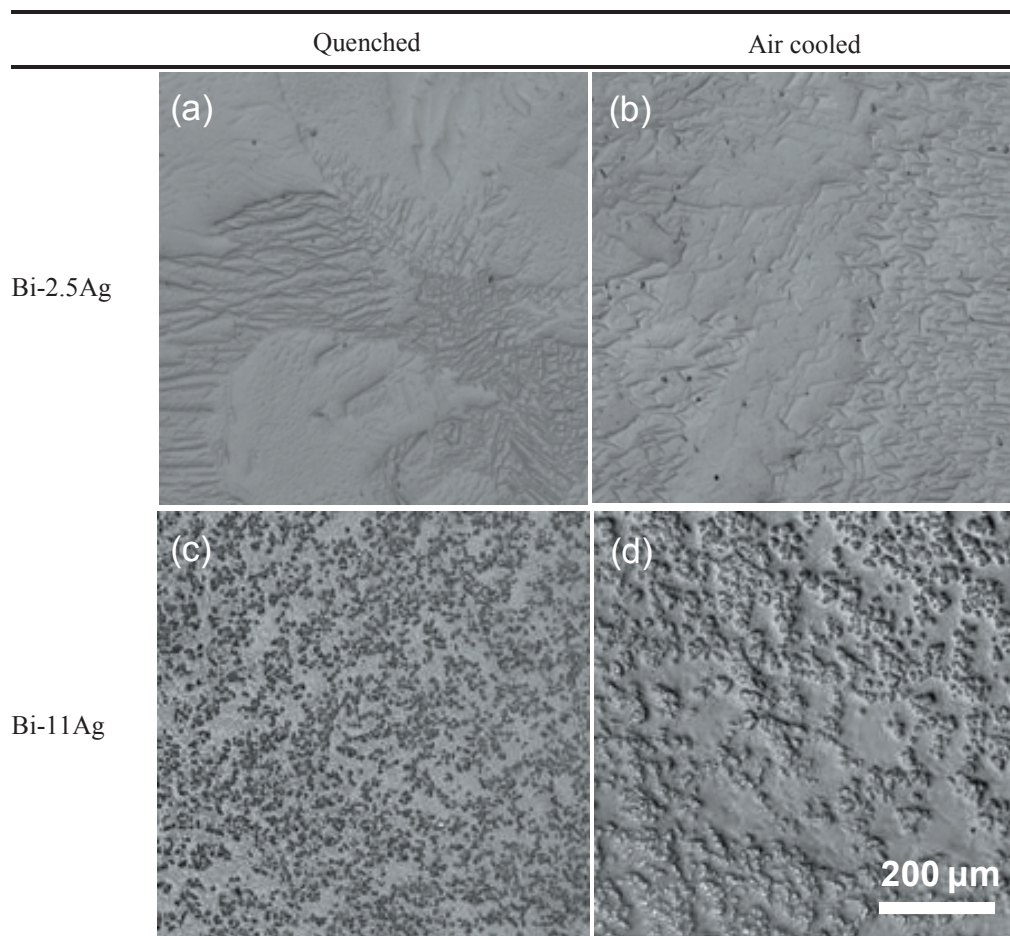
**Figure 3** shows the microstructure of the quenched and air-cooled Bi-2.5Ag and Bi-11Ag solder alloys. The microstructure of the Bi-2.5Ag solder alloy was independent of the cooling rate because the microstructure of the quenched specimen was quite similar to the air-cooled one as shown in **Fig. 3(a)** and **Fig. 3(b)**. On the other hand, the microstructure of the Bi-11Ag solder alloy depended on the cooling rate as shown in **Fig. 3(c)** and **Fig. 3(d)**. The size of each primary Ag phase, dark granulation in **Fig. 3(c)** and **Fig. 3(d)**, in the air-cooled specimen was greater than that in the quenched specimen. The density of primary Ag phase in the air-cooled specimen seems to be smaller than that in the quenched one. In addition to this, the distance between adjacent primary Ag phase in the air-cooled specimen also seems to be larger than that in the quenched specimen.

Both the size of primary Ag phase and the distance between adjacent primary Ag phase in the Bi-Ag solder alloys were measured as shown in **Table 2**, in order to quantify the above results. From **Table 2**, the average size of the primary Ag phase in the air-cooled specimen was about 18  $\mu\text{m}$  and was about three times as large as

those in the quenched specimen. Moreover, the average distance between adjacent primary Ag phase in the air-cooled specimen was about 112  $\mu\text{m}$  and this was about 1.6 times as large as that in the quenched specimen. Therefore, the microstructure of the Bi-11Ag solder alloy was affected by the cooling rate. The tensile test for the quenched and air-cooled B-2.5Ag and Bi-11Ag solder alloys were conducted in order to investigate the dependence of ductility on the solidification rate.

**Table 2** Size of primary Ag phase and the distance between adjacent primary Ag phase in the Bi-11Ag solder alloy

|            |                                            | Average | Maximum | Minimum |
|------------|--------------------------------------------|---------|---------|---------|
| Quenched   | Size of primary Ag phase                   | 6       | 15      | 2       |
|            | Distance between adjacent primary Ag phase | 72      | 121     | 37      |
| Air-cooled | Size of primary Ag phase                   | 18      | 34      | 2       |
|            | Distance between adjacent primary Ag phase | 112     | 243     | 51      |



**Fig. 3** Microstructure of Bi-Ag solder alloys of (a) quenched Bi-2.5Ag, (b) air-cooled Bi-2.5Ag, (c) quenched Bi-11Ag, (d) air-cooled Bi-11Ag.



Figure 4 shows the elongation of quenched and air-cooled Bi-Ag solder alloys. The elongation of the air-cooled Bi-2.5Ag solder alloy was quite similar for the quenched one, and its average value was about 1 %. On the other hand, the elongation of the air-cooled Bi-11Ag solder alloy was much larger than that of the quenched one, its average value was about 20 %. In order to elucidate the fact that the ductility of the Bi-11Ag solder alloy was improved by lowering the cooling rate, the fracture surface of the quenched and air-cooled Bi-11Ag solder alloys was investigated by using SEM.

The quenched specimen possessed a smooth flat cleavage surface as shown in Fig. 5(a). When Bi-11Ag solder alloy was air-cooled, the fracture morphology suggested that the alloys became more ductile because of the rough distorted surface with small facet, Fig. 5(b). existed on the fracture surface. Therefore, the main role of dispersed soft Ag primary phase is believed to act as the arrester of propagating cracks by dispersion in Bi matrix with appropriate size and distance, which improved ductility.

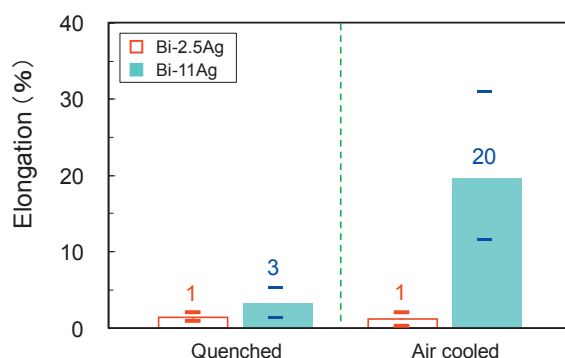


Fig. 4 Tensile elongation of Bi-Ag solder alloys of quenched and air-cooled.

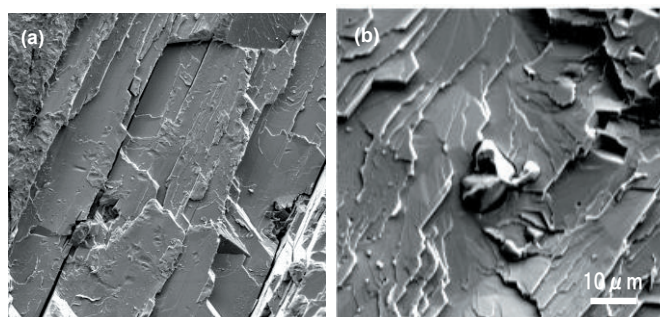


Fig. 5 Fracture surface of Bi-11Ag solder alloys of (a) quenched and (b) air-cooled.

#### 4. Conclusions

The mechanical properties of lead-free Bi-Ag solder alloys were investigated using tensile tests because the Bi-Ag solder alloys were relatively high melting temperature solders with reflow resistance. The obtained important results are summarized as follows.

- (1) The tensile strength gradually increased with increase of Ag content, the value reached about 40 MPa in B-11Ag solder alloy. The elongation showed the minimum at eutectic Bi-2.5Ag solder alloy, less than 2 %, and it only slightly increased with increase of Ag content up to 11 %Ag for quenched alloys.
- (2) The elongation of Bi-11Ag alloy was about 3 % showing brittle nature of this system. On the other hand, air cooled Bi-11Ag alloy showed improved elongation about 20 %, the value is much higher than that of quenched one, about 3 %. The dispersed Ag phase with average size of 18 μm was believed to act as an effective arrester against propagating cracks.
- (3) The hypereutectic Bi-11Ag solder alloy can be used as reflow resistant relatively high melting temperature solder materials having relatively good wettability and mechanical properties, especially it showed elongation of 20 % under air cooled condition.

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