Materials Transactions, Vol. 43, No. 8 (2002) pp. 1808 to 1815
Special Issue on Lead-Free-Electronics Packaging

Mechanical Properties and Microstructure of Tin–Silver–Bismuth Lead-Free Solder

Hanae Shimokawa, Tasao Soga and Koji Serizawa

Packaging Technology Center, Production Engineering Research Laboratory, Hitachi Ltd., Yokohama 244-0817, Japan

This paper presents the mechanical properties and microstructure of Sn–Ag–Bi Pb-free solder. We evaluated the effects of Bi content on the mechanical properties of Sn–Ag–Bi solder such as tensile strength, elongation and deformation behavior at cross-head speeds of 0.1 mm/min and 500 mm/min. The experimental results show that at low cross-head speeds, the addition of Bi to Sn–Ag solder initially increases the tensile strength and decreases elongation due to solid-solution hardening of Sn-phase. As the Bi content is increased to 10 mass% and more, however, elongation increases to a maximum at Sn–Ag–Bi solder containing 57 mass%Bi. Deformation of Sn–Ag solder is governed by slip within the Sn phase, and for high-Bi solders (about 57 mass%Bi) deformation occurs due to slip at Sn–Bi grain boundaries. Intermediate-Bi solders, on the other hand, do not slip in either the Sn phase or at Sn–Bi grain boundaries. At high cross-head speeds, the elongation of both intermediate-Bi solders and high-Bi solders was low and almost constant, indicating slip at Sn–Bi grain boundaries becomes difficult. The impact resistance of these solders was investigated through charpy impact tests, and it is found that Bi has a marked effect on impact resistance. The impact absorption energy of Sn–Ag solder decreases rapidly with the addition of Bi.

(Received March 8, 2002; Accepted May 21, 2002)

Keywords: *lead-free solder, tensile strength, elongation, impact resistance*

1. Introduction

Tin-lead solders such as Sn–37 mass%Pb (37Pb) are widely used in industry to fabricate electronic equipment. In the light of environmental and health concerns, however, efforts to develop Pb-free soldering technology have been made worldwide. Sn–Ag–Bi Pb-free solder is one of the possible alternatives to 37Pb solder due to its relatively high wettability and moderate melting point. However, since Bi is generally considered to be hard and brittle, it is important to evaluate the mechanical properties of Sn–Ag–Bi solders that contain this element.[1)]

In this study, we investigated the effects of Bi content in Sn–Ag–Bi solders on such mechanical properties as tensile strength and elongation at two different strain rates, and the mode of deformation was elucidated based on microstructure observations. These behaviors were considered from the viewpoint of solidification segregation and change in the lattice constant of the Sn phase. We also evaluated the effect of Bi content on the impact resistance of Sn–Ag–Bi solders to assess the practical applicability of these solders to products such as mobile electronics.

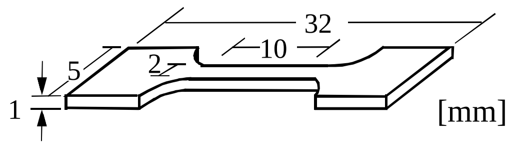

Fig. 1 Dimensions of tensile test specimens. Solder composition and temperature of carbon mold.

Table 1 Solder composition and temperature of carbon mold.

Solder composition (mass%) (abbreviation)	Temperature of carbon mold (K)
Sn–3.5Ag (3.5Ag)	553
Sn–3Ag–5Bi (5Bi)	
Sn–3Ag–10Bi (10Bi)	533
Sn–2.8Ag–15Bi (15Bi)	
Sn–2Ag–32Bi (32Bi)	
Sn–1Ag–57Bi (57Bi)	473
Sn–1Ag–70Bi (70Bi)	593
Bi	
Sn–37Pb (37Pb)	523

2. Experimental Procedure

2.1 Specimen preparation

Sn–Ag–Bi solders were melted in crucibles on a hot plate and poured into carbon molds. The specimens were then cooled to room temperature at a cooling rate of approximately 1 K/s, which is similar to the cooling conditions in actual soldering processes. The dimensions of the specimens are shown in Fig. 1. As implied above, the reason for preparing specimens only by casting is that the way in which the specimens are prepared greatly affects the mechanical properties of solders.[2,3)] To investigate the mechanical properties of solders in the joints between the electronic circuit board and electronic components usually fabricated only through the process of heating and cooling using a furnace, specimens were prepared by solidification in the carbon molds without machining or rolling. Solder composition and carbon mold temperature values are listed in Table 1. The Ag content was reduced with increasing Bi content along the Sn–Ag binary eutectic line.[4)] Specimens were aged at room temperature for 10 days after casting.

2.2 Tensile tests

Tensile tests were carried out using an Instron mechanical testing machine (4204) at cross-head speeds of 0.1 mm/min and 500 mm/min at room temperature to obtain tensile strength and elongation until failure. To investigate the deformation behavior of the solders, the specimens were prepared by finally polishing them with 0.25 µm diamond paste. We then observed the microstructure of specimen surfaces before and after the tensile tests by scanning electron microscopy (SEM).

2.3 Measurement of lattice constant

The lattice constant of the Sn phase was analyzed by an X-ray method using tensile test specimens. Using an X-ray diffraction meter developed by Mac Science Co, Ltd., we exposed the specimens to CuKα radiation.

2.4 Measurement of the eutectic region precipitation ratio

Solder composition of Sn–1Ag–45Bi and Sn–2.5Ag–20Bi were added for this measurement. DSC (Differential Scanning Calorimetry) curves of solders were measured using a calorimeter developed by Rigaku. Prior to DSC analysis, the solders were melted in a reflow furnace with a typical reflow soldering profile, in which cooling rate was about 1 K/s, since the solidification condition influences the appearance of the eutectic region with a low melting point in solder. After the reflow process, a 3.6 mg piece of solder was subjected to DSC analysis with a heating speed of 2 K/min. The endothermic calorie value at about 411 K was measured and its ratio to the endothermic calorie value of Sn–1Ag–57Bi was taken as the precipitation ratio of the eutectic region, as shown in Fig. 2.

2.5 Impact tests

Impact tests were carried out at room temperature and at 223 K using a charpy impact test machine developed by Tokyokoki Co., Ltd. Solder composition for the tests was 3.5Ag, 32Bi, and 57Bi (see Table 1), Sn–3Ag–1Bi (1Bi) and Sn–3Ag–3Bi (3Bi). The shape of the test pieces conformed to the JIS Z2202-5 (U notch) standard. The U notch size was 5 mm in length and 2 mm in width.

3. Results and Discussion

3.1 Mechanical properties and deformation behavior at low strain rate

3.1.1 Mechanical properties at low strain rate

Figure 3 shows the tensile strength and elongation of Sn–Ag–Bi solders tested at a cross-head speed of 0.1 mm/min. The addition of Bi initially increases the tensile strength and decreases elongation, however, as the Bi content is increased to 10 mass% or more, elongation increases to a maximum at 57Bi. The 57Bi solder has a near ternary eutectic composition with a fine eutectic microstructure, as shown later. Elongation decreases again at higher Bi content, but returns to a slightly higher value at 100%Bi. The tensile strength becomes maximum at about 10 mass%Bi, and gradually decreases as the Bi content increases in the range from 10 to 100%Bi.

From the observation of the morphology of fractured tensile test specimens of Sn–Ag–Bi solders, the specimens of Sn–Ag–Bi solders with low elongation, such as 10Bi and 15Bi, did not neck at all. The specimens of 32Bi and 57Bi, however, show necking in the parallel part.

3.1.2 Initial microstructure of Sn–Ag–Bi solders

To investigate the reason elongation is not proportional to the Bi content, as expected due to the hard and brittle nature of Bi, we examined the microstructure of the solders before and after the tensile tests. The observation results are shown in Fig. 4, in which the direction of tensile distortion is also shown. Figures 4(1)–(8) show the initial microstructure of each composition, and Figs. 4(9)–(16) show the microstructure change after the tensile tests. Identical areas were observed before and after the tests for 5Bi, 10Bi, 15Bi, 32Bi, 57Bi, and 70Bi specimens.

The initial microstructure of 3.5Ag consists of a Sn phase surrounded with dispersed Ag_3Sn, as shown in Fig. 4(1). These Sn phases precipitate as a primary crystal. As the solid solubility of Ag in Sn is very small according to the Sn–Ag binary phase diagram, the Sn phase consists almost entirely of Sn, which is confirmed later. It is found that Bi particles can be seen around the Sn phase in the initial 5Bi specimen, and that the 10Bi and 15Bi solders have more Bi particles around the Sn phase than 5Bi solder.

In the initial 32Bi specimen, there are two types of mi-

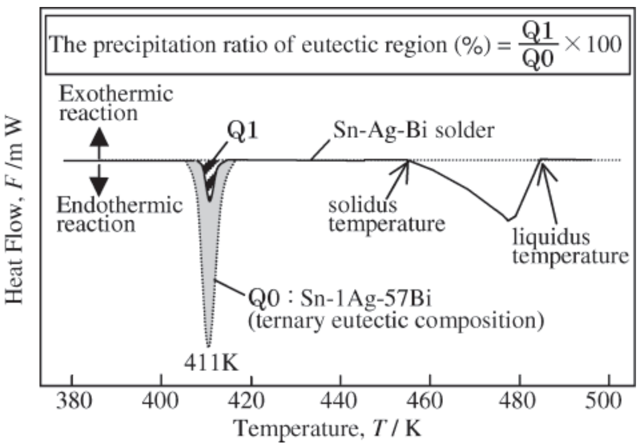

Fig. 2 Method of measuring precipitation ratio of eutectic region in Sn–Ag–Bi solder.

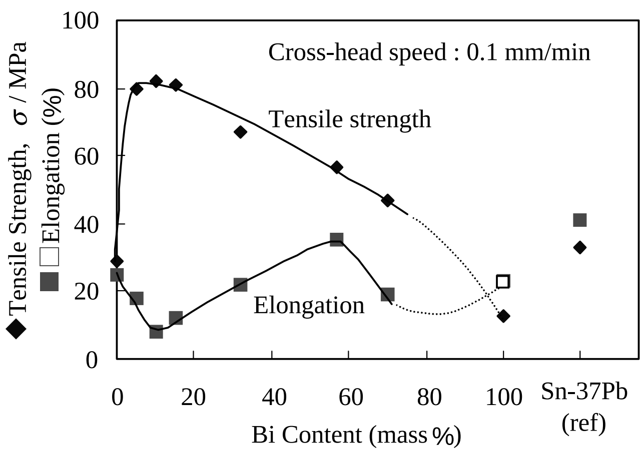

Fig. 3 Effect of Bi content on tensile strength and elongation of Sn–Ag–Bi solder.

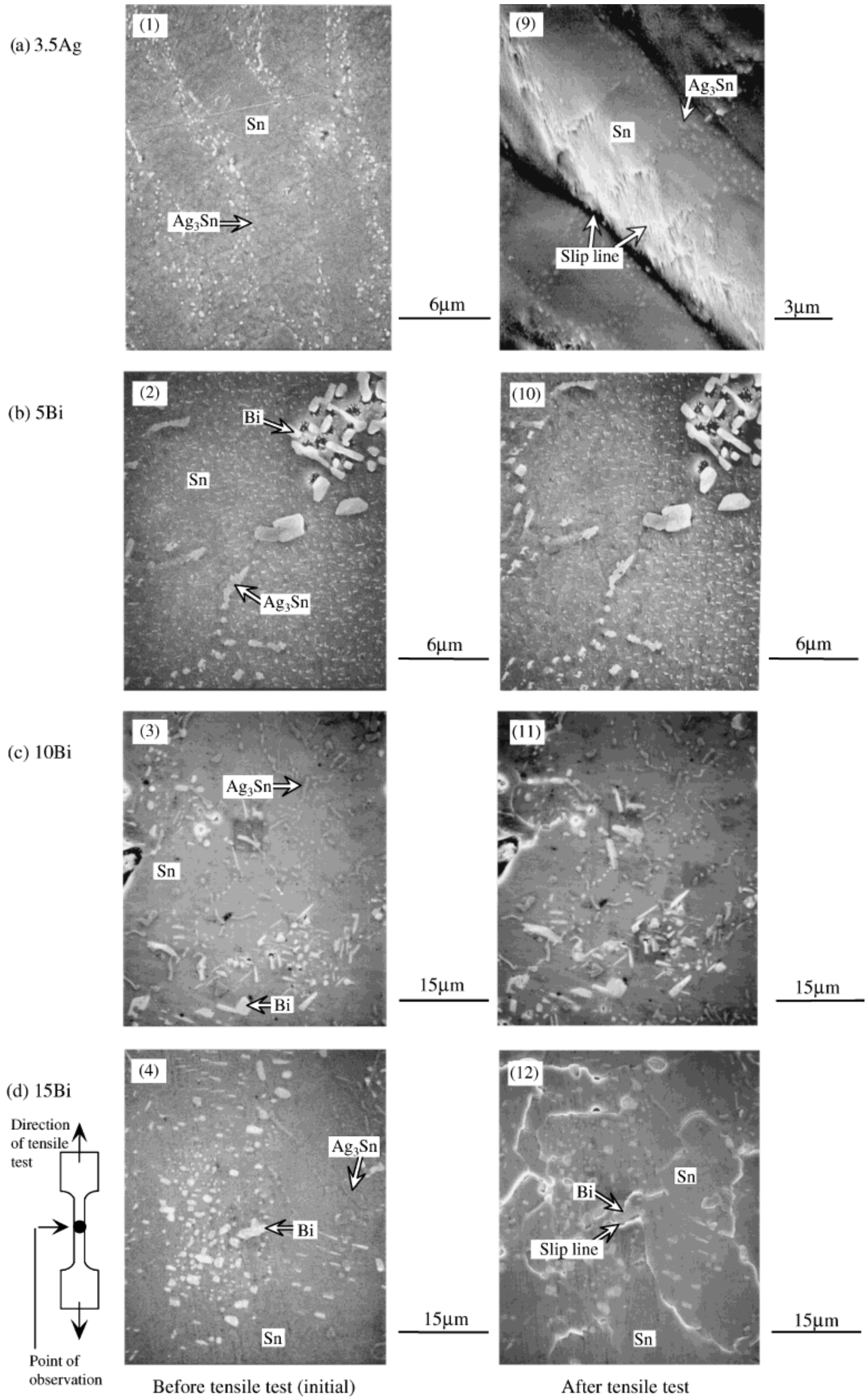

Fig. 4

crostructure, shown as areas (a) and (b) in Fig. 4(5). Area (a) is the primary crystal of the Sn phase containing finely dispersed Bi particles, and area (b), around the primary crystal of Sn, is eutectic Sn–Ag–Bi. The initial microstructure of 57Bi is a fine eutectic Sn–Ag–Bi structure, as shown in area (c) of Fig. 4(6), although a few primary crystals of Sn can still be observed in area (d). In the 70Bi specimen, a large primary crystal of Bi can be observed. Although Ag is not

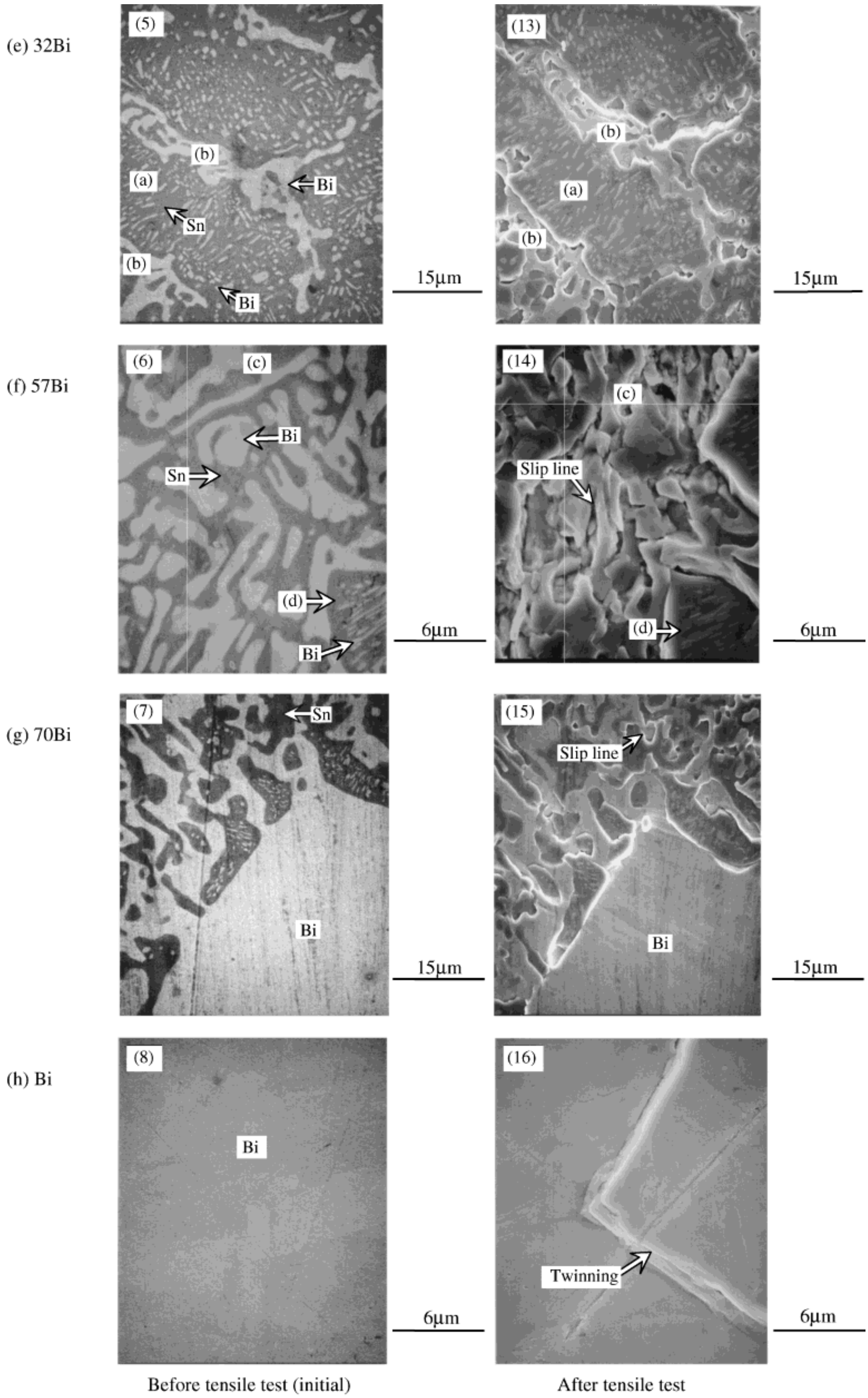

Fig. 4 Deformation behavior of Sn–Ag–Bi solders in tensile test.

clearly observed in Figs. 4(5)–(7), due to its low concentration, the eutectic region may consist of (Sn), (Bi) and Ag_3Sn according to the phase diagram.[4)]

3.1.3 Deformation behavior of Sn–Ag–Bi solders at low strain rate of 0.1 mm/min

Here, we will first discuss the deformation behaviors of Sn–Ag–Bi solders with relatively high elongation *i.e.*, those with

3.5Ag, 57Bi and Bi.

Following the tensile tests, the 3.5Ag solder, which has relatively high elongation, is found to exhibit slip lines through the Sn phase, as shown in Fig. 4(9). This indicates that the deformation of 3.5Ag solder is governed by slip inside the Sn phase, which consists almost entirely of Sn.

In the 57Bi solder, which also shows relatively high elongation in spite of the high Bi content, area (c) of the eutectic Sn–Ag–Bi region clearly changes more than area (d) of the primary Sn crystal containing finely dispersed Bi, as shown in Fig. 4(14). In area (c), slip appears to occur at the grain boundary between the Sn and Bi phases. Figure 5 shows the microstructure change at another point of an identical 57Bi specimen after the tensile tests. This figure also indicates that slip occurs at the grain boundary between the Sn and Bi phases. These observations indicate that the relatively high elongation of 57Bi solder is due to slip at the Sn–Bi grain boundary. It also indicates that Sn phases can not deform, probably due to precipitation hardening by Bi. Thus, it can be concluded that 57Bi solder deformation is due to slip at grain boundaries.

For 100%Bi, the behavior shown in the tensile tests is different from that of other Sn–Ag–Bi solders. First of all, the stress-strain curve of 100%Bi differs from that of other solders, as shown in Fig. 6. During tensile tests, the strength dropped rapidly and recovered many times, accompanied by audible sounds. The Bi specimens with low elongation of 12% show a large microstructure change, as seen in Fig. 4(16). These significantly different behaviors are thought to be due to deformation twinning. Furthermore, although the average elongation in eight separate tests was 23%, there was a wide variation in the elongation value, *i.e.*, from 8% to 79%. It is considered that this variation is related to the angle between the fractured surface and the direction of applied stress. Figure 7 shows the edges of two fractured tensile test specimens. Specimen (a) shows 79% elongation, and the angle between the fractured surface and the direction of applied stress is about 60°, whereas in specimen (b) with 9% elongation, the angle is almost 90°. The Bi specimens with low elongation tend to fracture in a direction vertical to the direction of applied stress. A similar phenomenon has been reported for single-crystal Bi wires, and the conclusion was that the variation of elongation is related to the variation of crystal orientation and single-crystal Bi wires with a cleavage angle of less than 57° exhibit high elongation.[5] Although our specimens are poly-crystal rather than single-crystal,[6] it is considered that a similar phenomenon occurred. Figure 7 also shows that both of the fractured surfaces are flat, indicating cleavage fracture without dependence on elongation. Therefore, the deformation of Bi is dependent on the crystal orientation, however the fracture mode is considered to be brittle with cleavage occurring due to low stress.

We next discuss deformation behaviors of Sn–Ag–Bi solders containing 5 to 32 mass%Bi and 70Bi, in which elongation is not very high. The sequence of discussion is from 70Bi to 5Bi.

For 70Bi, as shown in Fig. 4(15), the deformation occurs in the Sn–Ag–Bi eutecic region rather than in the Bi phase, and slips at the Sn–Bi grain boundary are observed. Therefore, the dominant parameter for the deformation of Sn–Ag–Bi solders with Bi content of more than 57 mass% is associated with Sn–Bi grain boundary slip. In addition, it is considered that the elongation and tensile strength decrease from that of 57Bi

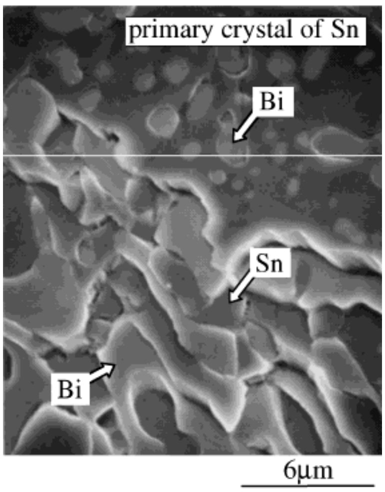

Fig. 5 Microstructure of 57Bi specimen surface after tensile test.

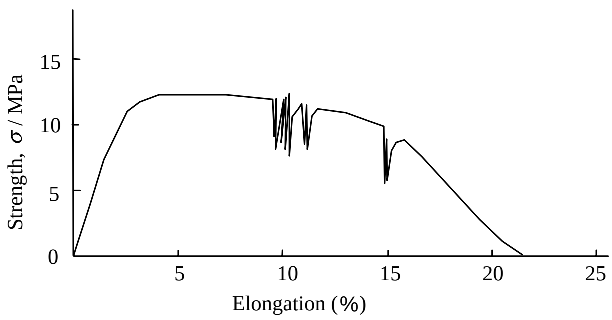

Fig. 6 Stress-Strain curve of Bi tested at 0.1 mm/min.

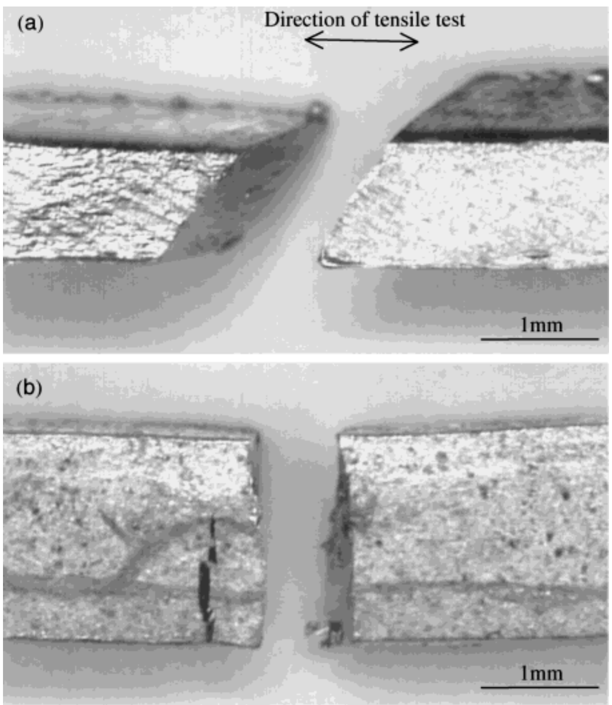

Fig. 7 Edge of fractured tensile specimen of Bi.

because primary crystals of Bi appear and the proportion of eutectic Sn–Ag–Bi decreases.

For 32Bi solder, as shown in Fig. 4(13), little deformation is observed in area (a), which is a primary crystal of Sn phase finely dispersed with Bi, whereas in area (b) the eutectic Sn–Ag–Bi region exhibits large deformation at the Sn–Bi grain boundary. This indicates that a decrease in the proportion of the eutectic Sn–Ag–Bi region helps to keep elongation lower than that seen in 57Bi, and that an increase in the proportion of primary crystal of the Sn phase with finely dispersed Bi particles helps to achieve a tensile strength higher than that of 57Bi.

As shown in Fig. 4(12), 15Bi solder shows deformation along the Bi particles, but it would seem difficult for this phenomenon to occur because of the amount of Bi being lower than 32Bi. In 10Bi and 5Bi solders, as shown respectively in Figs. 4(11) and (10), although there are Bi particles around the Sn phase, they do not appear to contribute to deformation because of their low concentration. Furthermore, no deformation in the Sn phase is clearly observed, as 3.5Ag deformation due to slip in the Sn phase is. Therefore, intermediate-Bi solders between 5 and 32Bi show low elongation and high tensile strength, since these solders do not slip in the Sn phase and the proportion of the Sn–Ag–Bi eutectic region decreases.

In this case, the inflection point to increase elongation is at about 10 mass%Bi, as indicated in Fig. 3. If the amount of Sn–Ag–Bi eutectic region is the dominant parameter of deformation for Sn–Ag–Bi solders, this result does not agree with the precipitation range shown in the Sn–Ag–Bi phase diagram.[4] According to this diagram, for Sn–Ag–Bi solders containing less than about 20 mass%Bi, the Sn–Ag–Bi eutectic region can not precipitate and Bi should exist in the Sn phase. As shown above in the initial microstructure of 5Bi, 10Bi and 15Bi, the precipitation of Bi outside the Sn phase probably depends on the solidification segregation with coring structure owing to a faster cooling rate than that in the equilibrium phase diagram. Figure 8 shows the precipitation ratio of the eutectic region with a melting point of 411 K measured by DSC. It is found that there is the region melts at 411 K in Sn–Ag–Bi solders containing less than 20 mass%Bi, which corresponds to the area where Bi particles precipitate around Sn phases in the initial microstructure. We also found that the inflection point to increase elongation at about 10 mass%Bi is identical to the starting point of precipitation of the eutectic region. Furthermore, the precipitation ratio of the eutectic region is proportional to the elongation of Sn–Ag–Bi solders containing between about 10 to 70 mass%Bi. These results indicate that a fine eutectic structure contributes to deformability occurred by grain boundary slip.

Since Sn is generally considered to be soft, it would seem that an increase in the amount of Sn would make solder more ductile. However, the results stated above do not support this. Therefore, we tried to explain this discrepancy by means of the change in lattice constants of the Sn phases. Figure 9 shows the lattice constants of the Sn phases as a function of Bi. The lattice constant of 3.5Ag is almost the same as that of Sn shown in a JSPDS (Joint Committee on Powder Diffraction Standards)-PDF (Powder Diffraction File), where the lattice constant of a is 0.5831 nm and that of c is 0.3182 nm. This indicates that the Sn phase in 3.5Ag consists almost entirely

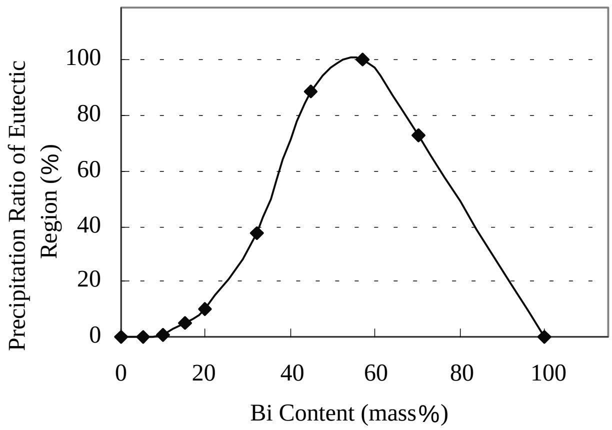

Fig. 8 Precipitation ratio of eutectic region in Sn–Ag–Bi solder.

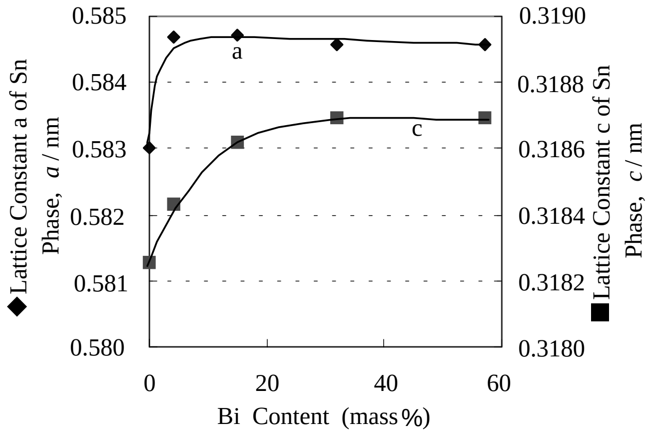

Fig. 9 Effects of Bi content on lattice constant of Sn phase.

of Sn. This result agrees with Sn–Ag phase diagram showing that the solubility of Ag in Sn is very low. The lattice constant of the Sn phase in 5Bi and 15Bi solders differs from that of 3.5Ag. From the fact that the solubility of Ag in Sn is very low again, and from the Sn–Ag–Bi phase diagram,[4] it is considered that Bi solutes in the Sn phase[7–9] and causes solid solution hardening of the Sn phase. These results are almost identical to those reported by Takemoto *et al.*[9] In addition, the lattice constant of the Sn phase became almost constant at more than 20 mass% because of saturation of Bi in the Sn phase, corresponding to the Sn phase with finely dispersed Bi particles in the microstructure of 32Bi, 57Bi and 70Bi. Therefore, in Sn–Ag–Bi solders with 10 to 57 mass%Bi, an increase in the Sn amount does not contribute to an increase in elongation, due to solid solution hardening. Furthermore, Sn–Ag–Bi solders ($<$ 5 mass%Bi), where the influence of the solid solution hardening of the Sn phase is small, will show high elongation because deformation can occur in the Sn phase.

We examined deformation behavior of 37Pb, the eutectic solder of the Sn–Pb system for comparison. The result is shown in Fig. 10. In 37Pb, slip lines can be seen through both the Sn and Pb phases, indicating that deformation in 37Pb occurs as a result of slip within the Sn and Pb phases rather than at grain boundaries.

The deformation of Sn–Ag–Bi solders is summarized as follows;

1) In Sn–Ag solder, deformation is governed by slip inside the

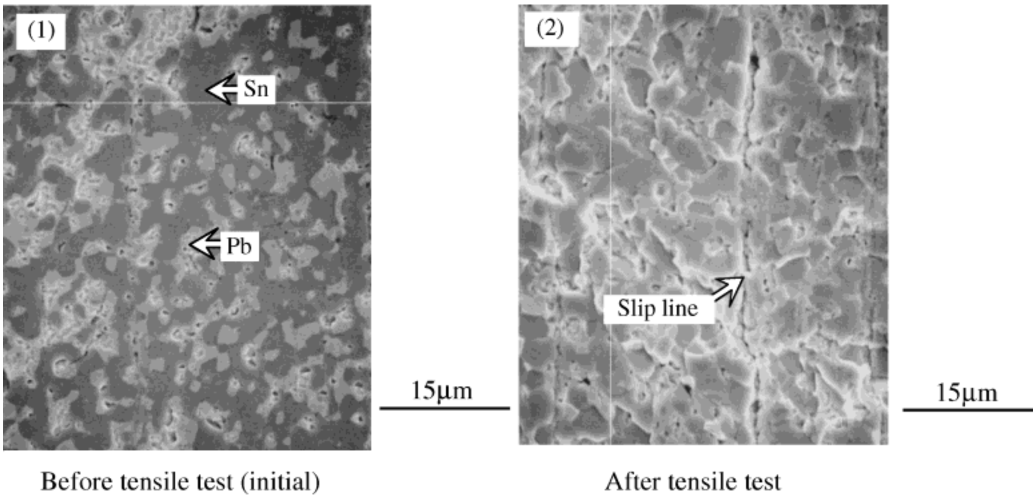

Fig. 10 Deformation behavior of Sn–37Pb solder in tensile test.

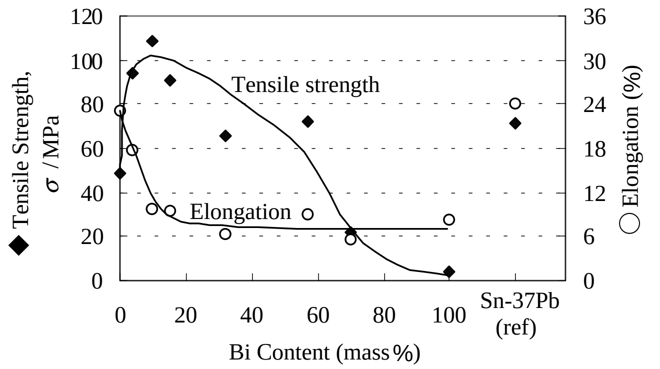

Fig. 11 Tensile strength and elongation at cross-head speed of 500 mm/min.

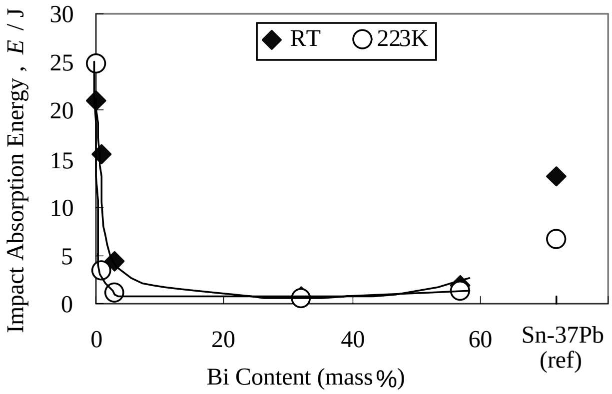

Fig. 12 Effect of Bi content on impact absorption energy of Sn–Ag solder.

Sn phase, which is not solid-solution hardened.
2) In high-Bi Sn–Ag–Bi solders (about 57 mass%Bi), deformation is due to slip at Sn–Bi grain boundaries.
3) In intermediate Sn–Ag–Bi solders (from 5 to 32 mass%Bi), deformation due to slip within the Sn phase or at Sn–Bi grain boundaries cannot easily occur. A primary crystal of Sn with Bi solid solution results in higher tensile strength.
4) The deformation behavior of Bi is different from that of other Sn–Ag–Bi solders.

Consequently, low-Bi Sn–Ag–Bi solders (<5 mass%Bi), where the influence of the solid solution hardening of the Sn phase is small, and high-Bi Sn–Ag–Bi solders (about 57 mass%Bi) are potentially useful in low strain rate applications, as high elongation is an important factor for such applications.

3.2 Mechanical properties at high strain rate

Figure 11 shows tensile strength and elongation tested at a cross-head speed of 500 mm/min, corresponding to a strain rate of approximately $8 \times 10^{-1}\,s^{-1}$. Elongation decreases only with the addition of Bi, in contrast to the low strain rate results. As Bi content is higher than 15 mass%, the elongation is low and almost constant. From the observation of the morphology of a fractured tensile test specimen of Sn–Ag–Bi solders tested at 500 mm/min, the Sn–Ag–Bi solders such as 32Bi and 57Bi no longer show necking, although they show necking in the 0.1 mm/min test. It is known that the mechanical properties of Bi bearing solders are likely influenced by the strain rate.[10] It is considered that deformation no longer occurs due to slip at the grain boundary between the Sn and Bi phases at high strain rates.

3.3 Effect of Bi content on impact resistance of Sn–Ag–Bi solder

The impact absorption energy at room temperature and at 223 K is shown in Fig. 12. It can clearly be seen that the addition of Bi rapidly reduces the impact absorption energy of the solder. Figure 13 shows the morphology of the test pieces after the impact tests. The 3.5Ag test pieces did not fracture at either room temperature or at 223 K, whereas the 1Bi test pieces fractured at 223 K and the 3Bi test pieces fractured at both room temperature and at 223 K. The impact absorption energy of 37Pb and the morphology of the test pieces are similar to that of 1Bi, and 37Pb test pieces did not fracture at room temperature but fractured at 223 K. The 57Bi solder exhibits a very brittle fracture mode even at room temperature. Figure 14 shows SEM images of the fracture surfaces for the 223 K test. The fracture surface of 37Pb is clearly dimpled, whereas the fracture surface of Bi-containing solders is not dimpled but cleavage is observed. These results indicate that the addition of Bi to Sn–Ag solder reduces impact resistance and

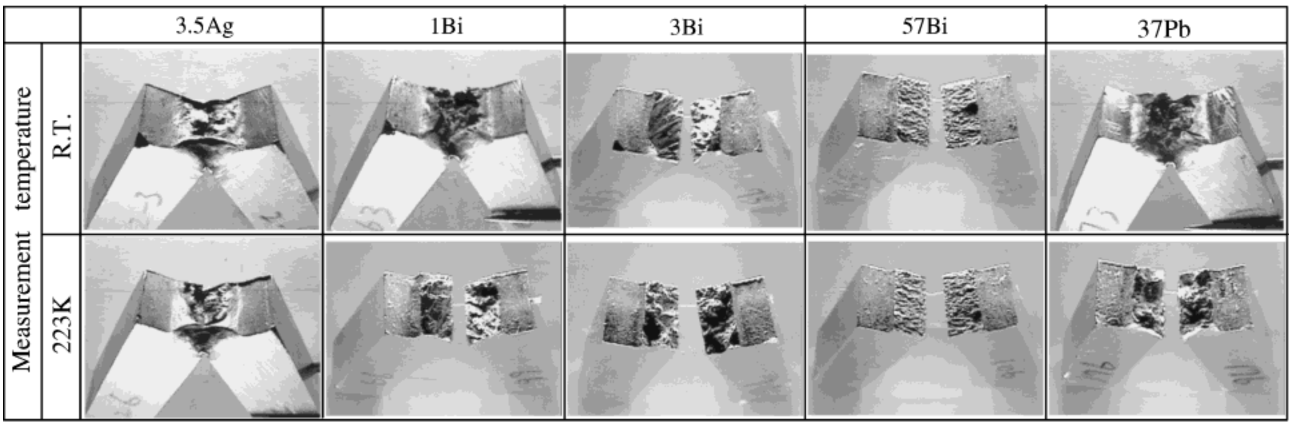

Fig. 13 Morphology of test pieces after impact test.

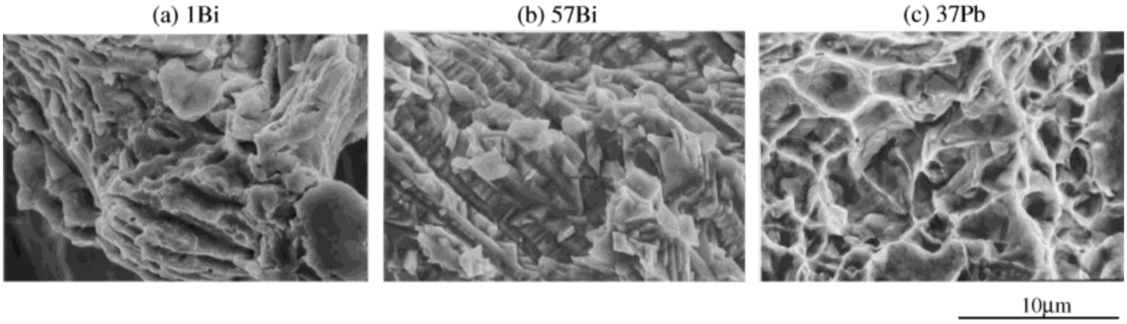

Fig. 14 Fracture surface of specimens after impact test at 223 K.

makes the solder extremely brittle under low temperatures. Thus, high-Bi Sn–Ag–Bi solder is not suitable for joints that are expected to incur high strain rates, such as those induced by rapid heating and cooling or by impact.

4. Conclusion

The effects of Bi content on the mechanical properties of Sn–Ag–Bi solder were investigated. The results can be summarized as follows:

(1) At low cross-head speed, the addition of Bi initially decreases elongation, however, as the Bi content is increased to 10 mass% or more, elongation increases to a maximum at 57Bi.

(2) The deformation of Sn–Ag solder is governed by slip inside the Sn phase, and the deformation of solder with about 57 mass%Bi is due to slip at Sn–Bi grain boundaries. Slip does not easily occur within the Sn phase or at grain boundaries in intermediate-Bi Sn–Ag–Bi solders, since Sn phase is solid-solution hardened and the proportion of the Sn–Ag–Bi eutectic region decreases.

(3) At high cross-head speed, the elongation of both intermediate-Bi solders and high-Bi solders was low and almost constant.

(4) The impact absorption energy of Sn–Ag solder was reduced significantly by the addition of Bi.

REFERENCES

1) K. Atsumi, Y. Kariya and M. Otsuka: Proc. 6th Symposium on Microjoining and Assembly Technology in Electronics, (2000) pp. 281–286.
2) R. Satoh, M. Oshima, K. Hirota and I. Ishi: Bulletin J. Japan Inst. Metals **23** (1984) 1004–1013 (Japanese).
3) R. Satoh, M. Oshima, K. Arakawa and K. Hirota: J. Japan Inst. Metals **49** (1985) 26–33 (Japanese).
4) U. R. Kattner and W. J. Boettinger: J. Electronic Materials **23** (1994) 603–610.
5) G. Motoyasu, H. Kadowaki, H. Soda and A. McLean: J. Materials Sci. **34** (1999) 3893–3899.
6) H. Sudo, I. Tamura, T. Nishizawa: *The Microstructure of Metals*, (Maruzen, Tokyo, 1972) pp. 16.
7) J. Hu, H. Tanaka, O. Munegata, T. Taguchi and T. Narita: Proc. 5th Symposium on Microjoining and Assembly Technology in Electronics, (1999) pp. 409–414.
8) J. A. Lee and G. V. Raynor: Proc. Phys. Soc. **B67** (1954) 737–749.
9) T. Takemoto, M. Takahashi, A. Matsunawa, R. Ninomiya and H. Tai: Quarterly Journal of the Japan Welding Society **16** (1998) 87–92 (Japanese).
10) J. Glazer: J. Electronic Materials **23** (1994) 693–700.