Formation Mechanism of Eutectic Cu₅Sn₅ and Ag₃Sn after Growth of Primary β-Sn in Sn-Ag-Cu Alloy

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In Sn-Ag-Cu solder balls, unusual microstructures consisting of both Sn-Ag₃Sn and Sn-Cu₅Sn₅ binary eutectic structures are sometimes observed. However, the formation mechanism of these unusual microstructures is still unclear. Therefore, in this study, the solidification process has been investigated to clarify the nucleation and growth of binary and ternary eutectic structures in Sn-1.0Ag-0.5Cu alloy by using thermal analysis and interruption tests.

Sn-Ag-Cu alloy.1,2) This alloy comprises two faceting compound phases—Ag₃Sn and Cu₅Sn₅—and the non-faceting Sn phase; this is in contrast to the Sn-Pb alloy, which is composed of two non-faceting phases—Sn and Pb.

Sn-Ag-Cu alloys have been already used as solder balls, but there are still some problems, such as the presence of large intermetallic compounds. Large Ag₃Sn or Cu₅Sn₅ are undesirable for solder alloys because their formation can be related to crack initiation, which may lead to serious reliability problems.3–5) As a primary phase, β-Sn is preferable to intermetallic compounds (IMCs) in the solder alloy. So far, various studies on the cooling rate, alloy content, and minor alloying elements have been carried out in order to avoid the growth of large IMCs.6–9)

Another serious problem is that the structures of Sn-Ag-Cu alloy are significantly more complex than those of traditional Sn-Pb solders. Sn-Ag-Cu alloys used as solder balls usually consist of β-Sn, Sn-Ag₃Sn or Sn-Cu₅Sn₅ binary eutectic structure and Sn-Ag₃Sn-Cu₅Sn₅ ternary eutectic structure. There is often some primary Ag₃Sn or Cu₅Sn₅ as well. However, an unusual microstructure consisting of both Sn-Ag₃Sn and Sn-Cu₅Sn₅ binary eutectic structures is sometimes observed.10) This unusual microstructure is known as a “double binary eutectic” structure. According to the phase diagram, these structures cannot be expected. The ternary eutectic structure should have as large a volume fraction as possible in the solder alloy in order to maintain high mechanical performance. However, it is difficult to control the volume fraction of the ternary eutectic structure because sometimes the double binary eutectic structure forms. Therefore, in this study, the solidification process was investigated by using thermal analysis and interruption tests to clarify the nucleation and growth of binary and ternary eutectic structures after the formation of β-Sn as a primary phase.

2. Experimental Procedure

Figure 1 shows the liquidus projection of the Sn-Ag-Cu phase diagram, calculated using Pandat (a computer-based tool). A NIST (National Institute of Standards and Technology) solder database for commercial solder alloys was used.11) According to this phase diagram, the eutectic point is at Sn-3.75 mass% Ag-0.9 mass% Cu, which is expressed in this article as Sn-3.75Ag-0.9Cu.

The Sn-1.0Ag-0.5Cu alloy, where β-Sn forms the primary phase, was used in this study. This alloy was prepared from pure Sn, Ag, and Cu, each of which had purities of 99.99 mass%. The expected solidification path calculated using Pandat is indicated by the arrows in Fig. 1.
Figure 2 illustrates a principal part of the experimental equipment. Ar gas was introduced from the top of the furnace to prevent the specimen from oxidizing. A specimen weighing approximately 5 g was put in an alumina crucible with inner and outer diameters of 12 and 16 mm, respectively. The temperatures of the furnace and specimen were measured by alumel-chromel thermocouples. The specimen was melted and then cooled in the electric furnace at a cooling rate of 0.05°C/s. The specimen was dropped into a water bath to quench the solid/liquid interface at various temperatures during cooling.

A cross section of the solidification structure was then observed. After polishing by alumina slurry, the specimens were further polished using colloidal silica, if necessary. After coating with platinum, the specimens were then observed with a field emission scanning electron microscope (FE-SEM) and analyzed by an energy dispersive X-ray spectroscopy (EDS).

### 3. Experimental Results

#### 3.1 Observation of final solidification structure

Figure 3(a) shows a typical solidification structure in the Sn-1.0Ag-0.5Cu alloy. There are some β-Sn dendrite arms and eutectic structures between them. Figures 3(b) and (c) show the EDS mapping results for Ag and Cu. The region where the concentration of Ag is high corresponds to eutectic Ag₅Sn. Similarly, the region where the concentration of Cu is high corresponds to eutectic Cu₆Sn₅. A backscattered electron (BSE) image of Fig. 3(a) is shown in Fig. 3(d). Since the brightness of this image corresponds to the atomic number, the phases can be easily distinguished. The white, round crystals are β-Sn, the light-gray crystals are eutectic Ag₅Sn, and the dark-gray crystals are eutectic Cu₆Sn₅. It is impossible to distinguish the primary β-Sn from the eutectic β-Sn based on this observation. The primary β-Sn was judged from its shape and size. Henceforth, BSE images were used to classify eutectic structures.

Judging from the distribution of eutectic Ag₅Sn and Cu₆Sn₅, the “eutectic structures” can be classified into three types: Sn-Ag₅Sn binary eutectic, Sn-Cu₆Sn₅ binary eutectic, and ternary eutectic. The schematic diagram is shown in Fig. 3(e), which corresponds to Figs. 3(a)–(c).

#### 3.2 Results of interruption test

A typical cooling curve of Sn-1.0Ag-0.5Cu alloy cooled at 0.05°C/s is shown in Fig. 5. No change, e.g., recalescence, was observed until the temperature in the specimen decreased to around 210°C at a constant rate. An enlarged portion of the cooling curve is indicated in Fig. 6. The recorded temperature increased abruptly to 223°C, and decreased again. A small change in the cooling rate occurred at about 220°C, and the temperature decreased to 216°C. It then increased to 216.7°C and remained unchanged for a while. The temperature decreased again after the specimen solidified completely. The cooling curve indicated two recalescences, the respective undercoolings being 13°C and 1°C.

The specimens were quenched at various points, which are indicated by dotted lines (a)–(e) in Fig. 6. Since the solidification rate before quenching was much smaller than that during quenching, the solidification structures were easily distinguished. Specimens were then metallographically analyzed to determine which phases or structures formed at the time of quenching.

Figure 7 shows BSE images of the solidification structure. Figure 7(a) indicates that there were very fine dendrites of β-Sn and interdendritic eutectic formations. Therefore, only a liquid phase is believed to have existed at point (a). The solidification structure, which was interrupted at point (b) in Fig. 6, is shown in Fig. 7(b). Here, the size of β-Sn dendrites was large. Thus, the recalescence was caused by nucleation and growth of β-Sn. Furthermore, there was a liquid phase in the interdendritic region at this point. The solidification structure quenched at point (c) in Fig. 6 is shown in Fig. 7(c). Here, there were coarsened dendrites of β-Sn and quenched liquid. However, the eutectic structure was not yet observed at this point. In a specimen quenched at point (d) in Fig. 6, there were coarsened dendrites of β-Sn and Sn-Cu₆Sn₅ binary eutectic structure and fine eutectic structures, as shown in Fig. 7(d). Since the formation of Sn-Cu₆Sn₅ binary eutectic structure had already begun at point (d), the inflection point in the thermal history corresponded to nucleation of eutectic Cu₆Sn₅. Eutectic Ag₅Sn was not yet observed at this point. The specimen remained at the eutectic temperature for some time (50 s). Finally, in the specimen quenched approximately 25 s after the temperature reached the ternary eutectic point (point (e) in Fig. 6), a ternary...
eutectic structure as well as dendrites of β-Sn and Sn-Cu₆Sn₅ binary eutectic structure were observed, as shown in Fig. 7(e). There were also some areas of Sn-Ag₃Sn binary eutectic structure in the specimen. Undercooling of about 1°C was found to be necessary for nucleation of the ternary eutectic structure, i.e., nucleation of eutectic Ag₃Sn.

4. Discussion

4.1 Solidification path simulated by Pandat and actual solidification process

In order to estimate the equilibrium solidification path of Sn-1.0Ag-0.5Cu, a Pandat Scheil simulation was performed. Figure 8 shows the simulation results. For this alloy, the equilibrium solidification path can be described as follows: L → primary β-Sn → Sn-Cu₆Sn₅ binary eutectic reaction → ternary eutectic reaction

Primary β-Sn forms at 226°C, Sn-Cu₆Sn₅ binary eutectic structure forms at 221.7°C, and finally the equilibrium solidification is terminated by the isothermal ternary eutectic reaction at 215.9°C.

In actual observations, primary β-Sn formed around 210°C, Sn-Cu₆Sn₅ binary eutectic structure formed around 220°C, and finally eutectic Ag₃Sn nucleated around 216°C, as shown in Figs. 6 and 7. Solidification did not start at the temperature estimated from the equilibrium phase diagram because of undercooling for nucleation. Furthermore, Sn-Ag₃Sn binary eutectic structure, which cannot be predicted by the equilibrium phase diagram, was observed in addition to ternary eutectic structures when the temperature in the specimen reached the ternary eutectic temperature. The formation of Sn-Ag₃Sn binary eutectic structure was not clearly detected in the thermal history shown in Fig. 6. These phenomena are discussed in 4.2.2.
4.2 Thermal history of Sn-1.0Ag-0.5Cu alloy

4.2.1 Formation of eutectic Cu$_6$Sn$_5$

Recalcescence was observed when $\beta$-Sn nucleated, after which $\beta$-Sn grew for a while. The slope of the cooling curve after the growth of $\beta$-Sn changed when Sn-Cu$_6$Sn$_5$ binary eutectic structure formed, as shown in Fig. 6. A detailed study was carried out to understand the formation of Sn-Cu$_6$Sn$_5$ binary eutectic structure. Figure 9 shows BSE images for the specimen’s microstructure when quenched at 221$^\circ$C and 220$^\circ$C at points (i) and (ii), respectively, in Fig. 6. As shown in Fig. 9(a), a fine eutectic structure was observed between coarsened dendrite of $\beta$-Sn. However, Cu-enriched zone was observed around the solid/liquid interface of $\beta$-Sn as indicated by the broken circle in Fig. 9(a). Therefore, eutectic Cu$_6$Sn$_5$ did not form down to a temperature of 221$^\circ$C.

In contrast, relatively coarse eutectic Cu$_6$Sn$_5$ was observed between $\beta$-Sn dendrite arms in the specimen quenched at 220$^\circ$C, as shown in Fig. 9(b). At the same time, Cu-enriched zones were no longer observed at this point. This directly indicates that the Sn-Cu$_6$Sn$_5$ binary eutectic solidification started in Cu-enriched zones, which are shown in Fig. 9(a).

4.2.2 Formation of eutectic Ag$_3$Sn

In this study, undercooling of about 1$^\circ$C was observed in the thermal history when ternary eutectic structures were
formed. Recalcescence occurred when eutectic Ag$_3$Sn nucleated because it did not exist before the specimen reached this temperature. However, the recalcescence for the second binary eutectic solidification was not observed in the thermal history. Therefore, the specimen was quenched at about 216°C (point (iii) in Fig. 6) in order to investigate the onset of the second binary eutectic solidification. Figure 10(a) shows the BSE image for the cross-section of the specimen. Based on the observation, eutectic structures were classified, and the classification diagram is superimposed on the photograph in Fig. 10(b).

Some areas of Sn-Cu$_6$Sn$_5$ binary eutectic structure are indicated by the blue line. Furthermore, some areas of Sn-Ag$_3$Sn binary eutectic structure are indicated by the red line. There were also quite fine eutectic structures that corresponded to the liquid phase when the specimen was quenched. Ternary eutectic structures formed as indicated by the yellow line, but Sn-Ag$_3$Sn binary eutectic structure did grow in the specimen when quenched after the recalcescence of ternary eutectic solidification. Thus, it can be concluded that the formation of Sn-Ag$_3$Sn binary eutectic structure started at the same time as the formation of the ternary eutectic structure.

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Fig. 7 BSE images of solidification structure on the cross-section of Sn-1.0Ag-0.5Cu alloy in the interrupted tests. The points quenched in the water bath are indicated in Fig. 6.

Fig. 8 Solidification path of Sn-1.0Ag-0.5Cu alloy obtained from a Pandat Scheil simulation.
The detailed mechanism for the formation of Sn-\(\text{Ag}_3\text{Sn}\) binary eutectic structure at the beginning of ternary solidification is not clear at present. However, the following mechanism can be considered. Figure 11(a) shows the enlarged SE image for the cross-section of the specimen quenched at point (d) in Fig. 6, and (b) and (c) show the EDS mapping results of Ag and Cu, respectively. As shown in Fig. 11(a), Sn-\(\text{Cu}_6\text{Sn}_5\) binary eutectic structure was observed in the center of the SE image. Some Ag-enriched zones were observed around the solid/liquid interface of Sn-\(\text{Cu}_6\text{Sn}_5\).
The composition of the remaining liquid at the ternary eutectic temperature may not be constant. If it is enriched by Ag as the Sn-Cu$_5$Sn$_5$ binary eutectic solidification proceeds, the ternary eutectic structure with high volume fraction of Ag$_3$Sn may be obtained, as shown in Fig. 4(d).

Similarly, if the composition of the remaining liquid is enriched by Cu, the ternary eutectic structure with high volume of Cu$_5$Sn$_5$ may be formed, as shown in Fig. 4(c). The reason that the ternary eutectic structures vary locally may be due to the fluctuation of the remaining liquid composition at the ternary eutectic structure.

5. Conclusions

In order to understand the solidification process after growth of primary $\beta$-Sn in Sn-Ag-Cu alloys, interruption tests using Sn-1.0Ag-0.5Cu alloy were performed. The following conclusions were obtained.

1) A Cu-enriched zone was observed around $\beta$-Sn in the liquid before Sn-Cu$_5$Sn$_5$ binary eutectic structure nucleated. Sn-Cu$_5$Sn$_5$ binary eutectic structure formed in these regions.

2) A Ag-enriched zone was observed around Sn-Cu$_5$Sn$_5$ binary eutectic structure in the liquid before formation of the ternary eutectic structure began. The unusual structure of Sn-Ag$_3$Sn binary eutectic structure formed in these regions just after the temperature reached the ternary eutectic point.

3) Ternary eutectic structures were classified into three types: ideal ternary structure, ternary eutectic structure with large volume fraction of Cu$_5$Sn$_5$ and ternary eutectic structure with large volume fraction of Ag$_3$Sn. These were due to the fluctuation of the remaining liquid composition at the ternary eutectic temperature.

REFERENCES