Evolution of Structure Unidirectionally Solidified Sn–Ag₃Sn Eutectic Alloy

Hisao Esaka, Kei Shinozuka and Manabu Tamura

National Defense Academy, Department of Materials Science and Engineering, 1-10-20 Hashirimizu Yokosuka, Kanagawa 239-8686, Japan

Sn–Ag₃Sn eutectic alloy is known as an attractive candidate to replace Sn–Pb soldering alloy. Since the solidified structure directly relates to the mechanical properties of joints, understanding of solidified structure of this alloy system is very important. Therefore, in order to understand the revolution of solidified structure, unidirectional solidification experiments have been carried out using eutectic Sn–Ag₃Sn alloy. When the growth velocity is larger than the critical value, Sn-dendrites solidifies as a primary phase. This is attributed to the skewed coupled zone in this alloy system. In this case, the volume fraction of the primary Sn increases with increasing growth velocity and approaches a constant. When the growth velocity is larger than the critical value, Sn-dendrites solidifies as a primary phase. This is attributed to the skewed coupled zone in this alloy system. In this case, the volume fraction of the primary Sn increases with increasing growth velocity and approaches a constant value. Interdendritic eutectic is composed with fibrous Ag₃Sn zone in this alloy system. In this case, the volume fraction of the primary Sn increases with increasing growth velocity and approaches a constant value. Interdendritic eutectic is composed with fibrous Ag₃Sn zone in this alloy system. In this case, the volume fraction of the primary Sn increases with increasing growth velocity and approaches a constant value. Interdendritic eutectic is composed with fibrous Ag₃Sn zone in this alloy system. In this case, the volume fraction of the primary Sn increases with increasing growth velocity and approaches a constant value.

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1. Introduction

Not only the health but also environmental concerns have demanded the development of lead-free solders. For this reason, many efforts have been made to search for suitable substitutes for the conventional Sn–Pb alloys. A Sn–Ag alloy has been recognized as one of the major candidates for lead-free solders. Since the eutectic temperature of Sn–Ag alloy (221°C) is still high, additions of other elements such as Bi, Cu, Sb and In are proposed as a third or fourth elements in order to lower the melting temperature. The solidified structures at the joint are very important to understand the mechanical properties of the electrical packaging. However, the solidified structure of above-mentioned alloys are very complex and various intermetallic compounds form.

Solidified structures in binary eutectic systems have been classified basically into 4 groups: regular-lamellar, regular-fibrous, irregular-lamellar and irregular-fibrous, depending upon the entropy of fusion and volume fraction. One can distinguish regular structure and irregular structure using the value of entropy of fusion (ΔSf) of both phases. One may also classify lamellar and fibrous because of the volume fraction of minor phase. Following this criterion, Sn–Ag₃Sn system is classified into irregular-fibrous eutectic, though the entropy of fusion of Ag₃Sn is not certain. The volume fraction of Ag₃Sn at the eutectic temperature is estimated approximately 5% from the equilibrium phase diagram. This value is much smaller than 14%, which is found in Al–Al₃Ni system, a typical fibrous eutectic alloy.

Unidirectional solidification experiments have been performed by the present authors changing both growth velocity and composition and stability of eutectic structure with changing composition and stability of eutectic structure with changing growth velocity in this alloy system. Therefore, the comparison of the interface temperature is very important in predicting the phase in a given solidification condition. However, the physical parameters in this eutectic system are unknown at present. As stated earlier, the revolution of solidified structure in eutectic Sn–Ag₃Sn alloy is very complex and not well understood. Therefore, this study is carried out to investigate the phase change in eutectic composition and stability of eutectic structure with changing growth velocity in this alloy system.

2. Experimental Procedure

Sn–3.5 mass% Ag alloy, which is the eutectic composition, was used in this study and prepared from pure Sn and Ag, the purity of which were 99.99 mass% respectively. An alloy was melted in an alumina crucible under argon gas flow. The molten metal was kept at 500°C for 1800 s and mixed with a quartz glass bar. Then the molten metal was sucked in a glass tube, the inner diameter of which was 4.5 mm. After sucking, the glass tube was immediately taken from the furnace and the molten metal was quickly cooled. The preparation method ensured the uniformity of the specimens.

Figure 1 illustrates a principle part of a unidirectional solidification apparatus. This is a typical Bridgman-type furnace, where the temperature gradient (G) and growth velocity (V) can be controlled independently. Ar gas is introduced from the top of the furnace to prevent the specimen from oxidation. The specimen was put in an alumina tube, the inner and outer diameters of which are 5 mm and 8 mm, respectively. The temperature of the furnace was measured by an alumel–chromel thermocouple, which was installed in the middle of the furnace.

The specimen was withdrawn downwards at a predetermined rate. To ensure the steady state, the withdrawing length was kept constant to be 100 mm. The growth velocities performed in this study were varied from 0.56 to 66.7 μm/s. The temperature gradient at around the eutectic temperature was 5.2 × 10³ K/m. After the withdrawal, the specimen was dropped into a water bath to quench the solid/liquid
The alumina tube was intentionally crushed when the specimen was fallen down in order to increase the cooling rate. The solidified structure was then observed on the longitudinal and transverse cross section. After polishing by alumina slurry, the specimen was deeply etched by dilute aqua regia between 240 to 600 s at room temperature. After coating with platinum, the specimen was then observed by a field emission scanning electron microscope (FE-SEM).

3. Experimental Results and Discussions

3.1 Morphology of solid/liquid interface

Typical solidified structures found in the longitudinal cross sections are shown in Fig. 2. The growth direction is from right to left. The growth velocities of them are 22.2 and 40.0 μm/s, respectively. The dark areas in these figures represent primary or eutectic Sn. Figure 2(a) is fully eutectic interface and there is no primary phase. Though a small amount of liquid phase remained when the specimen was quenched, the solid/liquid interface is easily judged from the morphology. Many fine eutectic Ag₃Sn are aligned along the growth direction. The macroscopic solid/liquid interface is slightly perturbed and exhibits the eutectic cell, because of inevitable impurities in the alloy and instability of the eutectic interface. Figure 2(b) shows the primary Sn-dendrites and following eutectic phase. The solid/liquid interface when the specimen was quenched can be judged from the morphology. The primary Sn-dendrites lead the eutectic solidification and eutectic phase exists interdendritic region. Since the crystallographic structure of Sn when it solidifies is body central tetragonal (b.c.t.), the preferred growth direction is known as [110]. Thus, dendrite arms are perpendicular to each other. Here again, the eutectic Ag₃Sn aligns along the heat flow direction and a macroscopic eutectic interface exhibits eutectic cell.

Figure 3 shows the transverse cross section of solidified structure. These cross sections are about 20 mm below the solid/liquid interface. The growth velocities of these are 22.2 and 66.7 μm/s, respectively. Figure 3(a) shows that elongated rods of eutectic Ag₃Sn aligned in Sn matrix. On the other hand, Fig. 3(b) shows the primary Sn-dendrite and interdendritic eutectic. In the eutectic region, many rods of eutectic Ag₃Sn are randomly dispersed in Sn matrix.

The reason that the primary Sn-dendrites appear even in the eutectic composition is due to a skewed coupled zone. The phase selection in this alloy system has been discussed elsewhere. It is believed that the phase, the interface temperature of which is the highest, would be selected in the unidirectional solidification condition. In this condition, the critical growth velocity for (eutectic) to (Sn-dendrite + eutectic) transition has been found to be 30 μm/s at a temperature gradient of 5.2 × 10³ K/m.

3.2 Characterization of primary Sn

3.2.1 Leading length of Sn-dendrite

A schematic drawing of a solid/liquid interface when some Sn-dendrites appear is shown in Fig. 4. There are Sn-dendrites and eutectic phase. Eutectic phase exists interdendritic region. Sn-dendrites and eutectic phase are aligned along the direction of heat flux. Since the positive temperature gradient is imposed, the distance between the tip of the Sn-dendrite and the eutectic interface (∆L) corresponds to the temperature difference between two interfaces. ∆L has been measured as a function of growth velocity.
Sn-dendrite does not appear, $\Delta L$ is defined to be zero. Figure 5 shows the relation between growth velocity and leading length ($\Delta L$). $\Delta L$ increases rapidly with increasing $V$. In this experimental condition, $V = 30 \, \mu m/s$ is the critical growth velocity for the transition from the eutectic interface to the Sn-dendrite interface. $\Delta L$ approaches about 400 $\mu m$ with increasing $V$ and remains constant.

Using the value of temperature gradient, the temperature difference between Sn-dendrite tip and eutectic interface is obtained to be 2.1 K when the growth velocity exceeds 40 $\mu m/s$. Burden and Hunt\(^{1,2}\) measured the thermal field during the unidirectional solidification of Al–Cu alloy and investigated the relationship between dendrite tip temperature and growth velocity. Esaka and Kurz\(^{13}\) have also measured the dendrite tip temperature using succinonitrile-acetone alloys. It is possible to determine the solid/liquid interface temperature from the change in the slope of temperature-distance curve, which is recorded by a thermocouple during unidirectional solidification. However, there are two difficulties to detect the temperature difference between the interfaces. Firstly, the change in the slope of temperature-distance curve when the second phase passes by the thermocouple is usually small, depending upon the amount of the second phase. Therefore, it is quite difficult to detect the interface temperature of the second phase. Secondly, there is a problem in the spatial resolution. In this study, the leading length of the Sn-dendrite is less than 400 $\mu m$. It is quite difficult or impossible to detect the interface positions of Sn-dendrite and eutectic interface because of the spatial resolution of the thermocouple. Therefore, the method depending on metallography, which has been applied in this study, is the most available to determine the temperature difference in interfaces of both phases.

### 3.2.2 Areal fraction of Sn dendrite

Through the observation of the transverse cross section with rather low magnification, the areal ratio has been measured using the image analyzer. In this measuring domain, there were at least 5 dendrite trunks. The areal ratio in this cross section equals to the volume fraction, since the direction of solidification is aligned and perpendicular to the observed area.

The change in areal fraction of Sn-dendrite ($\eta$) with growth velocity is shown in Fig. 6. When the growth velocity is less than 30.0 $\mu m/s$, $\eta$ remains zero, since there was no primary phase. On the other hand, when $V$ exceeds 30.0 $\mu m/s$, $\eta$ increases rapidly with increasing the growth velocity. However, $\eta$ does not continue to increase with increasing the growth velocity but it seems to approach a constant value, 30%.

In the case of equilibrium solidification, the volume fraction can be estimated with the lever rule when two phases appear during solidification. However, in the case of non-equilibrium solidification, it is not clear to evaluate the volume fraction of a phase during solidification. To evaluate the volume fraction of the primary Sn is uncertain when the coupled zone is skewed towards Ag-rich side as shown in this study.

The coupled zone is generally defined as the surrounded region by the extended liquidus lines. Even in the off-eutectic composition, the eutectic structure without any primary phase appears when the undercooling for growth of any primary phase is larger than that of eutectic phase. These ideas are schematically shown in Fig. 7. It is assumed that in the region of ‘primary Sn and eutectic’, the volume fraction of primary Sn is uncertain when the coupled zone is skewed towards Ag-rich side as shown in this study.

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According to the equilibrium phase diagram, the solubility of Ag in Sn is zero, therefore the value of $A$ in Fig. 7 is actually zero. The volume fraction of primary Sn reaches a constant value when the growth velocity is high as shown in Fig. 6. From this experimental result, the extended liquidus line for Ag$_3$Sn may go down straight as indicated in Fig. 7.

### 3.3 Morphology of eutectic Ag$_3$Sn

#### 3.3.1 Population of eutectic Ag$_3$Sn

One of the most important quantities for characterization of eutectic structure is the inter-lamellar spacing. However, since the solidified structure is irregular as shown in Fig. 3, it is rather difficult to define the spacing of eutectic pieces. Therefore, the number of pieces of eutectic Ag$_3$Sn per unit area ($\rho_e$) has been measured on the transverse cross section to characterize the solidified structure. Figure 8 shows the relationship between the growth velocity and the population of eutectic Ag$_3$Sn. In general, the population of Ag$_3$Sn increases with increasing the growth velocity. When the growth velocity is over 30.0 $\mu$m/s, which is shown with open circles, the slope with respect to growth velocity is rather small. In this region, the primary Sn-dendrite appears and the eutectic is a following phase. Using the least square regression analysis, the slope is obtained to be 1.13 in this region. Here, the change of the population of eutectic pieces in the growth velocity is approximately proportional to $V^{1.0}$. This indicates that the spacing between eutectic pieces of Ag$_3$Sn is proportional to $V^{-0.5}$. Thus, the growth of eutectic pieces is mainly controlled by the lateral solute diffusion at the solid/liquid interface. Since the cross section of the eutectic Ag$_3$Sn is round as shown in Fig. 3(c), the anisotropic character of Ag$_3$Sn may not be actualized. On the other hand, when the growth velocity is less than 30.0 $\mu$m/s, which is shown with solid circles in Fig. 8, the slope with respect to growth velocity is high. In this region, there is no primary phase. The slope is calculated by the least square regression method and is obtained to be 1.77. The power is much larger than unity. This indicates that the growth of eutectic Ag$_3$Sn is not determined only by diffusion of lateral solute diffusion at the solid/liquid interface. The structure of Ag$_3$Sn is reported to have a slightly rhombically deformed h.c.p., and it may exhibit a strong anisotropy. Therefore, the population of eutectic pieces of Ag$_3$Sn may strongly become small when the growth velocity is low.

#### 3.3.2 Aspect ratio of eutectic Ag$_3$Sn

Figure 9 shows the enlarged view of the eutectic structure on the horizontal cross section near the solid/liquid interface. The growth velocities of these are 0.56, 16.7 and 40.0 $\mu$m/s, respectively. When the growth velocity is 40.0 $\mu$m/s, the cross section of eutectic Ag$_3$Sn is round-shaped and randomly dispersed in the Sn matrix (Fig. 9(c)). On the other hand, when the growth velocity is 16.7 $\mu$m/s, the cross section of eutectic Ag$_3$Sn is rectangular and pieces of eutectic Ag$_3$Sn are unidirectionally aligned. Furthermore, when the
growth velocity is $0.56 \mu m/s$, the piece of eutectic $Ag_3Sn$ is completely plate-like and that is almost parallel to each other. Therefore, this seems to be lamellar structure. The aspect ratio of the pieces of eutectic $Ag_3Sn$ $(\gamma)$ observed on the transverse cross section is measured and shown in Fig. 10. When the growth velocity exceeds $30.0 \mu m/s$, the primary Sn-dendrite appears and the aspect ratio of eutectic $Ag_3Sn$ is almost constant and unity. When the growth velocity is less than $30.0 \mu m/s$, the aspect ratio increases with decreasing the growth velocity. When the growth velocity is less than $5 \mu m/s$, the aspect ratio is large enough and the eutectic $Ag_3Sn$ can be judged as a lamella.

Chadwick discussed on the morphological change in eutectic structure and showed that the minor phase of the eutectic changes from lamellar to fibrous with increasing growth velocity. He also pointed out that this transition would take place even when the volume fraction of minor phase is approximately 10%, such as Al–AlNi eutectic alloy. The volute fraction of $Ag_3Sn$ in Sn–$Ag_3Sn$ eutectic system is 5% and is smaller than that of AlNi in Al–AlNi eutectic system, though, lamellar-to-fibrous transition takes place. At the intermediate zone in growth velocity, the eutectic $Ag_3Sn$ exhibits an elongated fibrous shape or plate-like shape. This intermediate shape indicates that the intermetallic compound, $Ag_3Sn$, may have a strong anisotropy on the surface tension.

The present experimental results on the morphology of the eutectic $Ag_3Sn$ indicated that the eutectic $Ag_3Sn$ in the interdendritic region exhibits fibrous form. On the other hand, in the case of no primary phase, the aspect ratio of eutectic $Ag_3Sn$ increases with decreasing growth velocity. In order to check the influence of growth velocity on morphological change of the eutectic $Ag_3Sn$, the experiments using Sn–3.0 mass% Ag alloy have been performed. The experimental procedure is the same as that of the eutectic alloy.

The solidified structures on the transverse cross section when the growth velocity was $16.7 \mu m/s$ are shown in Fig. 11. It is recognized through the observation with low magnification (Fig. 11(a)) that there are primary Sn dendrites and interdendritic eutectic. Observation with high magnification (Fig. 11(b)) reveals that there are elongated pieces of eutectic $Ag_3Sn$ in the interdendritic region. Figure 12 shows that the morphological change in eutectic $Ag_3Sn$ observed on the transverse cross section in Sn–3.0 mass% Ag alloy. Figure 12(a) indicates the lamellae eutectic $Ag_3Sn$ when the growth velocity is $0.56 \mu m/s$. When the growth velocity is $16.7 \mu m/s$, eutectic $Ag_3Sn$ are elongated as shown in Fig. 12(b). Furthermore, when the growth velocity is $44.4 \mu m/s$, fibrous eutectic $Ag_3Sn$ are observed (Fig. 12(c)).

The aspect ratios of eutectic pieces are measured in Sn–3.0 mass% Ag alloy. The results are shown in Fig. 13. The experimental results obtained in Sn–3.5 mass% alloy are also shown in this figure. Though there is some scatter the experimental results obtained in Sn–3.5 mass% Ag alloy agrees with those in Sn–3.5 mass% Ag alloy. The transition velocity for morphological change of eutectic $Ag_3Sn$ has been found to be $30.0 \mu m/s$ at a temperature gradient of $3.5 \times 10^3 K/m$. Therefore, it can be concluded that growth velocity has the strong influence on the morphology of eutectic $Ag_3Sn$, regardless of the leading phase in unidirectional solidification.

4. Conclusions

In order to understand the evolution of the solidified structure of Sn–$Ag_3Sn$ system, unidirectional solidification
using a eutectic Sn–Ag alloy has been performed. The following conclusions have been obtained.

1) Leading length of the primary Sn-dendrite rapidly increases and remains almost constant with increasing growth velocity. This corresponds to the difference in the temperature of the interface.

2) Areal ratio of dendrite abruptly increases and remains constant with increasing the growth velocity. This indicates an asymmetrical coupled zone of this alloy system.

3) Aspect ratio of eutectic Ag₃Sn observed on the transverse cross section increases with decreasing the growth velocity. The change in the morphology of eutectic Ag₃Sn is attributed to the anisotropy of the surface tension of Ag₃Sn.

REFERENCES