Abnormal Grain Growth of Ni$_3$Sn$_4$ at Sn-3.5Ag/Ni Interface

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By the reaction of molten solder alloy with compositions of 96.5Sn-3.5Ag (compositions are all in weight percent unless specified otherwise) with either the thick Cu or the thick Ni substrate at 250 °C, the rounded Cu$_4$Sn$_5$ grains formed over Cu and the faceted Ni$_3$Sn$_4$ grains precipitated over Ni. As the soldering time changed from 1 min to 60 min, normal grain growth occurred for rounded Cu$_4$Sn$_5$ grains while abnormal grain growth (AGG) mode was observed for faceted Ni$_3$Sn$_4$ grains. The measured grain size distributions also confirmed the difference between normal grain growth and abnormal grain growth.

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1. Introduction

There are two largely different types of grain morphology in the intermetallic compound (IMC) that has been observed at the interface between Sn-based solders and metal substrates during liquid soldering. The IMC grains are mostly hemi-spherical or scallop-shaped and their surfaces are rough (rounded) on Cu while it is polyhedral-shaped and faceted on Ni.1–6)

According to the classical solidification theory of unary materials proposed by Jackson,7) the geometry of the surface that separates two types of atoms of liquid and solid may be faceted or meandering (rough), which is highly correlated with the Jackson’s parameter. The Jackson’s parameter of the crystal with a rough surface is smaller than 2 while it is larger than 2 for faceted grains.

Bearing in mind that the grain morphology of the IMC at the interface in the liquid soldering is similar to the morphology of the growing solid into the liquid, the solidification theory of unary materials has been extended to growth of binary or multicomponent IMCs between liquid solders and solid metals.8) Again, it has been observed even for the multicomponent interfacial reaction that the Jackson’s parameter of the IMC grain with a rough surface is smaller than or similar to 2 while it is larger than 2 for faceted grains. The thermodynamically calculated results agreed well with experimental observations.

As a result, it became interesting to study the growth behavior of IMC grains in the liquid soldering in terms of faceting because the AGG can occur when the solid/liquid interface is singular, i.e. faceted.9) In normal growth of grains, the grain size distribution (normalized to the average size) remains invariant for various periods.10,11) The grains are usually spherical or equiaxed with rounded shapes because of their rough surface structure.12–14) In AGG, some grains grow to larger sizes relative to the matrix grains and the grain size distribution becomes widely spread out. As the large grains grow into the regions of the fine matrix grains, they impinge on each other. When only the impinged large grains remain, the grain size distribution becomes narrow. AGG is thus characterized by changing grain size distribution (or equivalently, the lack of self-similarity in the grain microstructure).15–17) In this work, therefore, the grain growth behaviour of the IMCs at the interface between liquid solders and solid substrates will be studied in terms of AGG and the size distribution.

2. Experimental Procedures

The 96.5Sn-3.5Ag solder alloys were prepared from pure Sn and Ag metals of purity higher than 99.9%. They were encapsulated under vacuum in quartz tubes, melted and held at 800 °C for 30 min for mechanical mixing. As-cast alloys were obtained by cooling each melt in air. Then they were cold-rolled into a 0.1 mm thick sheet and punched in the form of a disk-type specimen (5 mm in diameter). These disk-type specimens were put on Cu and Ni substrates (purity higher than 99% and 0.5 mm thick). Both substrates were polished with 1 μm diamond paste and cleaned in acetone and ethanol solution. Soldering was performed in the molten state at 250 °C from 1 to 60 min using rosin mildly activated (RMA) flux. As-soldered specimens on the Ni substrate were quenched in water at room temperature and etched with 50 vol% HNO$_3$ solution to reveal the 3-dimensional morphology of IMC grains formed at the interface by removing the remaining solder. In case of the as-soldered specimens on the Cu substrate, the etching solution of 35 g/L orthonitrotoluene and 50 g/L NaOH was used.

The interface in the top view of the solder joint was examined by the scanning electron microscopy (SEM) operated at 10 kV. The phases formed at the interface were identified by the X-ray diffraction (XRD) analyses. The equivalent sphere diameters of the grains were measured by tracing micrographs using a digitizer connected to a personal computer. More than 200 grains were examined to measure the grain size distribution of the IMC phase.

3. Results and Discussion

On reaction of molten solder with solid copper, the IMC grains formed all over the surface of the copper. The IMC phase in Figs. 1(a–d) was identified as Cu$_4$Sn$_5$ by the X-ray diffraction (XRD) analyses shown in Figs. 2(a–d). The soldering temperature was 250°C and the soldering time...
changed as follows: 1, 5, 30 and 60 min from Fig. 1(a) to (d). According to Figs. 2(c,d), two types of IMC are observed, i.e., Cu₆Sn₅ and Cu₃Sn even if the solder element of Sn and the substrate element of Cu are excluded. The grains of another stable Cu₃Sn phase were not observed in the top-view SEM images because they precipitate after the precipitation of Cu₆Sn₅ and thus they are located below the Cu₆Sn₅ grains.²⁻⁴⁻⁵ Most grains are hemi-spherical and rounded except that few of them look faceted although it is not clear from the top-view micrographs. There is no sign of abnormally large grains during this period of soldering time.

As the soldering time increased from 1 to 60 min, the average grain size increased from 1.9 to 15.55 µm but the corresponding grain size distribution remained quite unchanged as seen in Fig. 3. Figure 3(a) shows the grain size distribution of 1 min soldering and Fig. 3(b) is true for 60 min soldering, both of which were normalized with respect to the average size. They are the same in nature because the relative standard deviation (normalized to the average size) is almost the same and the maximum grain size is about two times as large as the average size in both cases. Even from the size distribution there was no indication of AGG of the rounded Cu₆Sn₅ phase. They grew normally.

On the contrary, Figs. 4(a–d) show the abnormal growth behavior. Through XRD patterns shown in Figs. 5(a–d), it was identified as the Ni₃Sn₄ phase and they clearly show faceting. The soldering temperature was 250°C and the time changed in the same way of Fig. 1: 1, 5, 30 and 60 min from Fig. 4(a) to (d). Several grains started to grow abnormally, especially at Figs. 4(b) and (c), and ultimately one typical very huge grain survived at 60 min of Fig. 4(d).

The size distributions of faceted Ni₃Sn₄ grains shown in Figs. 4(a) and (d) are described in Fig. 6. There is a significant difference in the obtained size distribution between 1 min and

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**Fig. 1** Top-view SEM images of Cu₆Sn₅ grains formed between molten Sn-3.5Ag and Cu substrate during liquid soldering at 250°C for (a) 1 min, (b) 5 min, (c) 30 min and (d) 60 min. Solder was etched away to reveal the Cu₆Sn₅ grains. It shows normal grain growth.

**Fig. 2** XRD patterns of the interface in Sn-3.5Ag/Cu joints with soldering time for (a) 1 min, (b) 5 min, (c) 30 min and (d) 60 min. Soldering temperature was 250°C.

**Fig. 3** Measured equivalent sphere size distribution of rounded Cu₆Sn₅ grains that are shown in Figs. 1(a) and (d): (a) 1 min and (b) 60 min. X-axis was normalized to average size.
60 min. Fig. 6(a) shows the grain size distribution of 1 min soldering and Fig. 6(b) shows the case of 60 min soldering, both of which were normalized to the average grain size, too, as in the case of Fig. 3. As the soldering time increased from 1 to 60 min, the average grain size increased from 0.11 to 1.01 µm and the grain size distribution changed drastically to a widely spread-out type. Especially, in Fig. 6(b), the maximum grain size is greater than the average by more than ten times and the size distribution has a long tail. Because of the wide span in the x-axis the whole spectrum of the grain size was not shown but broken into several intervals. From the normalized size distributions obtained in Fig. 6, it can be concluded that AGG of the faceted Ni$_3$Sn$_4$ phase occurred.

The Jackson’s parameter of Cu$_6$Sn$_5$ and Ni$_3$Sn$_4$ are calculated in Table 1. Because $\xi$ is a fraction of the total number of nearest neighbors in a plane parallel to the interface under consideration and it is difficult to calculate the exact value of $\xi$ due to the random orientational relationship between adjacent IMC grains, a mean value of $\xi$, 0.5, was used. For example, the hexagonal Cu$_6$Sn$_5$ phase has $\xi$ equal to 0.5 for the close-packed plane (0001), which implies that even a value of 0.5 is a very large number that it can take. In the Sn-3.5Ag/Cu and the Sn-3.5Ag/Ni joints of this work, the Jackson’s parameter of Cu$_6$Sn$_5$ was obtained as 1.18 (smaller than 2) and that of Ni$_3$Sn$_4$ was 3.29 (larger than 2), respectively. As expected from these thermodynamic calculations, the surface of the Cu$_6$Sn$_5$ grains is rough while that of
the Ni$_3$Sn$_4$ phase is faceted, which has been observed in Figs. 1 and 4. It has been verified again that normal grain growth occurs when the solid/liquid interface is rough and the abnormal grain growth (AGG) can occur when the solid/liquid interface is faceted. This type of abnormal growth behavior has been observed in many pure metals such as Ag, Cd, Cu, Ni, Fe, Pb and Sn$^{18}$ as well as in many ceramic materials such as niobium carbide, tungsten carbide, silicon carbide, silicon nitride, alumina and barium titanate.$^{16}$ However, the AGG was first observed in intermetallic compound materials of this work. As mentioned earlier in this article, most Cu$_6$Sn$_5$ grains were rounded in this study but other researchers found out that some of the Cu$_6$Sn$_5$ grains showed apparent faceting.$^{19,20}$ Of course, it was not clear in this work. Because the mechanism of AGG is closely related to the anisotropic surface energy, the grains growing abnormally often develop elongated shapes, especially in the hexagonal systems.$^{15,17}$ The whisker formation of the faceted hexagonal Cu$_6$Sn$_5$ grains may also be related with AGG.$^{19}$

The faceted Ni$_3$Sn$_4$ grains showed a symptom of abnormal growth during extended liquid stage soldering in this study. In electronic packaging, however, this type of prolonged soldering is not practiced. Nonetheless, the solder joints experience at least three or four reflow cycles on mounting. There is a great possibility of change in interfacial microstructures during these repeated reflow cycles, especially when the Ni layer is used in the under bump metallurgy. The initial formation of the IMC at the interface means a good metallurgical bonding but the excessive growth and the abnormal grain growth behavior of IMC grains can strongly affect the subsequent solderability.

4. Summary

Upon reaction of molten 96.5Sn-3.5Ag solder alloy with either Cu or Ni substrate at 250°C, the rounded Cu$_6$Sn$_5$ grains formed on Cu and the faceted Ni$_3$Sn$_4$ grains precipitated on Ni. During liquid soldering from 1 min to 60 min, normal grain growth occurred for rounded Cu$_6$Sn$_5$ grains while abnormal grain growth (AGG) took place for faceted Ni$_3$Sn$_4$ grains. The corresponding grain size distributions also confirmed the difference between normal grain growth and abnormal grain growth.

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REFERENCES