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Dramatic morphological change of scallop-type Cu₆Sn₅ formed on 001... single crystal copper in reaction between molten SnPb solder and Cu

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Wetting reaction between molten Sn-based solders and Cu produces scallop-type Cu₆Sn₅. In the present wetting study, a 001 single crystal Cu is used as substrate and a dramatic change in the morphology of Cu₆Sn₅ is observed: instead of scallop type, the authors observed a rooftop-type Cu₆Sn₅ grains, elongated along two preferred orientation directions. This was confirmed by electron beam backscattered diffraction and white beam synchrotron x-ray microdiffraction. The results indicate that the nucleation, growth, and ripening behavior of Cu₆Sn₅ on single crystal substrate can be quite different from the conventional case of wetting on randomly oriented polycrystalline Cu substrates.

Because of the wide application of solder, especially Pb-free, in consumer electronic products, the study of the wetting reaction of molten solder on Cu has attracted considerable interests. Metallic bonding in solder joints is achieved through the formation of Cu-Sn intermetallic compounds of Cu₆Sn₅ and Cu₃Sn at the Cu/solder interface. The Cu₆Sn₅ has a unique scallop-type morphology, and the Cu₃Sn has a layer-type morphology. The latter forms between the former and the copper substrate. Figure 1 is a top-view scanning electron microscopy SEM image of Cu₆Sn₅ scallops on a polycrystalline Cu substrate after the remaining solder was etched away. The scallops appear rounded and there are deep channels between them. The crystal structure of the low temperature phase Cu₆Sn₅ is monoclinic. Our recent study using white beam synchrotron micro-x-ray diffraction showed that the formation of Cu₆Sn₅ on Cu has a set of preferred orientation relationships. There are six types of preferred orientation relationships between the two phases, and in all cases the 101 direction of Cu₆Sn₅ is parallel to the 110 direction of Cu. The six orientation relationships are as follows:

\[
\begin{align*}
(010)_{\text{Cu₆Sn₅}} &\parallel (001)_{\text{Cu}} \text{ and } [-110]_{\text{Cu₆Sn₅}} \parallel [110]_{\text{Cu}} & \text{1} \\
(343)_{\text{Cu₆Sn₅}} &\parallel (001)_{\text{Cu}} \text{ and } [-101]_{\text{Cu₆Sn₅}} \parallel [110]_{\text{Cu}} & \text{2} \\
(-343)_{\text{Cu₆Sn₅}} &\parallel (001)_{\text{Cu}} \text{ and } [-101]_{\text{Cu₆Sn₅}} \parallel [110]_{\text{Cu}} & \text{3} \\
(101)_{\text{Cu₆Sn₅}} &\parallel (001)_{\text{Cu}} \text{ and } [-101]_{\text{Cu₆Sn₅}} \parallel [110]_{\text{Cu}} & \text{4} \\
(141)_{\text{Cu₆Sn₅}} &\parallel (001)_{\text{Cu}} \text{ and } [-101]_{\text{Cu₆Sn₅}} \parallel [110]_{\text{Cu}} & \text{5}
\end{align*}
\]

This is because a low misfit of 0.24% between the Cu atoms can be achieved along the 01 Cu₆Sn₅ direction and the 110 Cu direction. The above relationships can be classified into two groups based on the strong pseudohexagonal symmetry around Cu atom in Cu₆Sn₅ when projected along the 01 direction Fig. 2. Crystal planes in Eqs. 1 - 3 correspond to edges of the Cu hexagon group 1 and Eqs. 4 - 6 correspond to diagonals of the Cu hexagon group 2.

Since the low misfit directions between Cu₆Sn₅ and Cu lie on the 001 plane of Cu, it is of interest to investigate the behavior of Cu₆Sn₅ formed on 001 single crystal Cu. Single crystal Cu substrates were purchased from Goodfellow and they have a diameter of 1 cm and a thickness of 0.25 cm. The surface was carefully polished, cleaned, and etched before being immersed in flux. Wetting samples were prepared by reacting small beads 0.5 mg of 55Sn45Pb in wt % solder with the 001 single crystal copper in flux at 200 °C with different reaction times ranging from 30 s to...
4 min. The molten solder forms a cap on the Cu upon wetting. After a given time of reaction, samples were quenched to room temperature by dipping them into acetone. After solidification, the unreacted solder was removed by mechanical polishing, followed by selective chemical etching in order to expose the interfacial Cu$_6$Sn$_5$ scallops.

Figure 3 shows the morphology of Cu$_6$Sn$_5$ formed on 001 Cu substrate. Elongated and rooftop-type Cu$_6$Sn$_5$ grains were distributed on the entire surface. The elongations go along two perpendicular directions. We hypothesized that Cu$_6$Sn$_5$ should elongate along the low misfit direction in order to minimize interfacial energy with Cu. Electron beam backscattered diffraction EBSD analysis was performed to verify the elongation direction. Because of the high roughness of the sample see Fig. 3, performing EBSD mapping is an issue. However, since each grain is a single crystal, a single Kikuchi pattern coming from a selected spot of an elongated grain is enough to determine its orientation. Kikuchi patterns were obtained separately from the 001 single crystal Cu substrate and Cu$_6$Sn$_5$ grains, and we found that Cu$_6$Sn$_5$ grains are elongated along two different 110 directions. Figure 4 a is a Kikuchi pattern from the Cu substrate. Figures 4 b and 4 c are the respective Kikuchi patterns of an elongated grain and of another grain perpendicular to the first one. The analysis indicated that the 001 plane of Cu is perpendicular to the surface normal, and that the 110 directions are nearly parallel within 4° to the laboratory x and y axes. The Kikuchi pattern shown in Fig.

Figure 5 a is a histogram of the angles between the 001 direction of Cu and the 101 direction of Cu$_6$Sn$_5$, after the 4 min reaction at 200 °C. An area of 25 30 m$^2$ was scanned with a step size of 0.5 m in both x and y directions. There is a strong peak at 90°, indicating that the 01 1 directions of most of the Cu$_6$Sn$_5$ scallops are lying on the 001 plane of Cu. Figure 5 b is a histogram of the angles between the 010 direction of Cu and the 101 direction of Cu$_6$Sn$_5$. There are two peaks: one peak is at 45° and the other is at 135°. It indicates that the 01 directions of most of the Cu$_6$Sn$_5$ grains are parallel to the 110 or 100 directions.
tion of Cu. The above results confirm the existence of a strong preferred orientation relationship between Cu₆Sn₅ and 001 Cu on the bases of EBSD and synchrotron micro-x-ray diffraction.

The dramatic change in morphology of Cu₆Sn₅ suggests that nucleation, growth, and ripening mechanisms of the elongated Cu₆Sn₅ can be different from the rounded scallop-type Cu₆Sn₅. Figure 6 is a SEM image of Cu₆Sn₅ scallops on 001 Cu after 30 s reflow. Clearly Cu₆Sn₅ already has very strong texture. The strong texture of Cu₆Sn₅ indicates that nucleation of the Cu₆Sn₅ is not random but rather oriented when 001 Cu is used as a substrate. Soldering is a reactive wetting. When molten solder spreads on copper dissolution of copper substrate takes place at the interface. If the orientation of substrate copper is a high-index hkl plane, more copper will be required to be dissolved away in order to expose the low misfit 110 crystal directions and 001 planes of Cu. Therefore, the nucleation of Cu₆Sn₅ will not have enough time to nucleate with the preferred orientation if the Cu substrate is a high-index plane, and random nucleation will become dominant. However, if the substrate is a 001 single crystal Cu, Cu₆Sn₅ can directly nucleate on the low misfit direction and plane. As a result, Cu₆Sn₅ grains will have an oriented nucleation and textured growth.

Due to the strong orientation relationship between the elongated Cu₆Sn₅ and 001 Cu, as shown in Fig. 3, we expect a lower interfacial energy between them than that between the round scallop-type Cu₆Sn₅ and polycrystalline Cu, as shown in Fig. 1. Indeed when we etched the Cu₆Sn₅, we found that the elongated Cu₆Sn₅ on 001 has lasted much longer in the etchant. The lower interfacial energy will improve the impact fracture toughness of the interface.

In summary, a dramatic change in morphology of Cu₆Sn₅ was found when Sn-based solder was reacted with a 001 single crystal Cu. Grains of Cu₆Sn₅ become elongated along the two low misfit directions between Cu₆Sn₅ and Cu. The relationship between the morphology and the crystallographic orientation was verified by EBSD study. Statistical distribution data obtained by white beam synchrotron micro-x-ray diffraction agreed with the EBSD study. The Cu₆Sn₅ already showed strong texture at 30 s of wetting reaction, indicating that the grains tend to nucleate with texture.

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