Joining of Copper Plates by Unusual Wetting with Liquid Tin and Tin–Lead Solder on “Surface Fine Crevice Structure”

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Previously, a surface fine crevice structure on a copper plate was created by laser irradiation and was found by the authors to be suitable for unusual wetting. Copper plates with surface fine crevice structure were joined by an unusual wetting phenomenon using liquid bismuth as joining material. In this study, we examined the viability of using tin and a tin–37 mass% lead solder as joining materials by focusing on intermetallic compound formation with copper. The wettability of the surface fine crevice structure on a copper plate by liquid tin and tin–lead solder was investigated and joint experiments were performed using two copper plates. The successful wetting of tin and solder material on the surface fine crevice structure of copper and the joining of copper plates was confirmed despite the formation of intermetallic compounds.


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1. Introduction

Tanaka and coworkers¹ discovered a brazing and soldering method for metal–metal joining by unusual wetting¹–³ on a fine porous surface structure, which is formed by atmospheric oxidation–reduction, with minimum overlay formation at the request of spatial limitations on printed circuit boards⁴,⁵. The authors⁶ found that a surface fine crevice structure, which consists of a structure looks like splashing water on the outermost surface and crevices formed at intervals of several tens of microns below the outermost surface, was created by laser irradiation of the copper (Cu) metal surface as shown in Fig. 1. This structure causes the unusual wetting of liquid bismuth (Bi). In addition, the joining of two Cu plates was achieved by unusual wetting of the fine surface crevice structure. Laser irradiation overcomes the inability to control the treated area by atmospheric oxidation–reduction to create a surface fine crevice structure in a target area, which results in region-selective unusual wetting. The research has focused on unusual wetting caused by capillary action based on only the wettability between Bi and Cu without any reactions and compound formation because intermetallic compounds do not exist in a binary Bi–Cu system, their mutual solubility is low at low temperature⁷ and liquid Bi wets solid Cu at the experimental temperature studied¹,⁸. In practical situations, however, brazing and soldering are conducted by dissolution and compound formation.

In this work, the wettability of a surface fine crevice structure of Cu by liquid materials, which react with Cu to form the intermetallic compounds, was investigated. Tin (Sn), which is the main component of soldering materials, and Sn–37 mass% lead (Pb) solder, which is a practical soldering material, were selected as liquid materials. From phase diagrams of the Cu–Sn⁹ and Cu–Sn–Pb¹⁰ systems (Fig. 2), it is predicted that intermetallic Cu and Sn compounds are formed. The joining of a laser-treated surface structure of metal Cu plates by unusual wetting of liquid Sn and Sn–Pb solder was attempted.

2. Wetting Experiments

2.1 Sample and methods

Cu plate of 2-mm thickness and 99.96% purity was used in the wetting experiments. Sn (99.999% purity) and a Sn–Pb-based eutectic solder (Sn–37 mass% Pb) were used as liquid materials. An yttrium aluminum garnet (YAG) laser (Miyachi Corporation, ML-7062A) was used. Cu plates were irradiated with Q-switched YAG laser with a 6.0 kHz pulse. The wavelength and output power were 1064 nm and 50 W, respectively. The sample position was adjusted to satisfy a 0.1 mm laser spot diameter. A 10 × 10 mm region on the Cu plate was irradiated in a reticular pattern with a scanning rate of 10 mm/s.

Fig. 1 Surface fine crevice structure of Cu created by laser irradiation.

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and a 0.05 mm scan interval. Before the experiments, a piece of Sn or solder was treated with 10% hydrochloric acid solution and cleaned ultrasonically using ethanol. The piece of Sn or solder was placed at the boundary between the laser-treated and normal surfaces on the Cu plate to compare the wettability of laser-irradiated surface by liquid Sn or solder with that of the normal surface. After positioning the sample in a soaking area in the furnace, residual air in the furnace was evacuated, and hydrogen (H₂) gas (99.995% purity) was introduced into the furnace. H₂ gas was dehydrated using silica gel and magnesium perchlorate. The experiment was carried out under 20 mL/min H₂ gas flow. The sample was heated to 673 K for 40 min. Sn and solder were completely melted at 673 K (the melting temperatures of Sn and solder are 505 and 457 K, respectively)\(^1\). Once the temperature reached 673 K, the sample was cooled at −10 K/min to room temperature. The contact angles of the solid Cu by liquid Sn are 37° at 510 K\(^1\), and 23°\(^1\) and 25°\(^1\) at 673 K, and those of solid Cu by liquid Sn–37 mass% Pb solder are 25° at 503 K\(^2\) and 23° at 543 K\(^2\). Both combinations provide a wetting system, i.e. a contact angle of less than 90°.

### 2.2 Results and discussion

The sample appearance before and after the wettability experiments using liquid Sn is shown in Fig. 3. Sn spreads throughout the laser-irradiated area whereas Sn does not spread to the normal surface, which means that Sn spreads preferentially to the laser-irradiated area after melting. This behavior is similar to that of Bi\(^3\). A scanning electron microscopy (SEM) cross-sectional view of the sample at the interface between Cu and Sn is shown in Fig. 4. The "surface fine crevice structure" changes its appearance. Several phases are thought to exist in the system based on the color contrast in the image. A new layer is formed on the crevice surface, and the water-splashing-like structure phase appears different from a new layer and plate. Elemental mapping by energy-dispersive X-ray spectroscopy (EDX) is shown in Fig. 4. Phases were confirmed based on elemental mapping and spot analysis by EDX. The dark phase, which is located in the lower part of the figure and shows periodical convex/concave shapes with an about 50 μm cycle, is Cu. The lighter phase that formed as a layer along the periodical convex/concave shapes of Cu is the ε-phase (Cu₃Sn). The other lighter phase that is dispersed in the remaining region is the η-phase (Cu₆Sn₅) and the light part is Sn. The compound formation observed in this work is assumed from the phase diagram of the Sn–Cu system and literature on research related to the Cu–Sn system\(^4,17\). In a sessile drop method, compound formation generated by reaction of a flat substrate with liquid material during wetting improves substrate wettability by a
liquid material\textsuperscript{18,19}). For complicated structures such as "surface fine crevice structure" and porous structures that cause capillary action, it is supposed that compound formation and growth can close the vacancies of these structures. This may interrupt the liquid capillary action. A comparison of Fig. 4 with the original "surface fine crevice structure" in Fig. 1 shows that the water-splashing-like structure of the fine surface crevice structure still remains even after the wetting experiment although compound formation proceeds. It is thought that liquid Sn infiltrates fine surface crevice structure vacancies faster than their clogging because of compound formation and following growth under these experimental conditions. From these results, it was found that unusual wetting of Sn occurs on the "surface fine crevice structure" of Cu in the face of the intermetallic compound formations.

Figure 5 shows the sample after wettability experiments using liquid Sn–Pb solder. As well as Sn, solder prefers to spread to the laser-irradiated area rather than to the normal surface after melting. A cross-sectional view at the interface between Cu and Sn–Pb solder of the sample by SEM is shown in Fig. 5. The "surface fine crevice structure" also changes its appearance like in the experiment with Sn. Several phases exist in the system. From the phase diagrams\textsuperscript{9–11), it is predicted that compounds similar to those in the wetting experiment with Sn appear because Pb does not form any intermetallic compounds with Cu and Sn. The phases were confirmed based on spot analysis by EDX. Compounds \(\varepsilon\)-phase (Cu\(_3\)Sn) and \(\eta\)-phase (Cu\(_6\)Sn\(_5\)) formed near and far from Cu, respectively, by the reaction of Cu and Sn of the solder alloy. Sn- and Pb-rich phases were also observed. These phases may be separated from solder alloy according to the phase diagram\textsuperscript{11) under cooling or Pb, that is not involved in the reaction of Cu and Sn, remains. Although interruption of the capillary action of solder because of clogging of vacancies in the fine surface crevice structure by compound formation and growth is a prominent concern, it is thought that solder alloy infiltrates the vacancies faster than the intermetallic compounds form and grow like Sn. Based on the above results, we found that
unusual wetting of a practical soldering material occurs on the "surface fine crevice structure" of Cu even though intermetallic compound formation occurs.

3. Joint Experiment

3.1 Sample and methods

An attempt was made to join two Cu plates to confirm the joint by unusual wetting caused on the "surface fine crevice structure". Sn (99.999% purity) was used as a liquid metal during joining. Two types of Cu plates with a "surface fine crevice structure" formed by laser treatment were prepared in the joint experiment. A 10 × 12 mm area on the 15 × 15 mm plate and the entire area on the 10 × 10 mm plate were irradiated by laser under the same conditions as the wetting experiments. As shown in Fig. 6, the laser-irradiated areas of the two plates were contacted, and Sn or Sn–Pb solder was placed at a point distant from the contact interface. The wetting experiment apparatus was also used here. After positioning the sample in a soaking region of the furnace, residual air in the furnace was removed by evaluation and H2 gas (99.995% purity) was introduced into the furnace. The experiment was carried out under 20 mL/min H2. The sample was heated to 773 K for 40 min. At 773 K, the sample was cooled at −10 K/min to room temperature.

3.2 Results and discussion

The sample appearance after the joint experiment for the two Cu plates with Sn and the cross-sectional contact area between the two plates are shown in Figs. 7 and 8, respectively. Sn spreads throughout the laser-irradiated area and infiltrates the gap between the two Cu plates. Several phases are confirmed at the gap between the two Cu plates and in the wetting experiment. A layer of ε-phase (Cu3Sn) is formed along Cu, and a η-phase (Cu6Sn5) exists aside from Cu and Sn. Figure 9 (a) shows the sample after joining the two Cu plates with solder. The solder spreads throughout the laser-irradiated area. The gap between the two Cu plates is filled with solder as shown in Fig. 9 (b). In both experiments, the two Cu plates were not detached even when the samples were rotated perpendicularly, which means that the two Cu plates were joined with Sn or Sn–Pb solder material. These results indicate that the joining of metal Cu plates can be achieved by unusual wetting on the "surface fine crevice structure" even in a system where liquid and solid materials react to form intermetallic compounds. As future works, the researches on the effects of amount of solder materials and compounds on joint strength are essential for the practical application of joining with unusual wetting on the "surface fine crevice structure". The solder filling at the joint should be assessed by considering not only the filling at the gap of materials but also the filling at the "surface fine crevice structure". In addition, it is known that the intermetallic compounds can affects the strength of joint20).

Fig. 6 Schematic joining experiment setup for two Cu plates. Laser-irradiated areas of upper and lower substrates in contact with each other, and Sn or Sn–Pb solder is positioned at a point distant from the terminal contact area.

Fig. 7 Appearance of sample after joining experiment with Sn.

(a) Cross section of sample after joining experiment with Sn and (b) magnified image with specified phases.
4. Conclusions

Unusual wetting with Sn and a practical soldering material (Sn–Pb eutectic solder) can occur on the "surface fine crevice structure" of Cu plate even when intermetallic compounds are formed. Cu metal plates were joined by the unusual wetting of Sn and Sn–Pb solder on the "surface fine crevice structure".

REFERENCES