Examination of improvement effect of surface modification of Cu with organic acid on solder paste wettability using a laser displacement meter†

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KEY WORDS: (solder paste) (wettability) (laser displacement meter) (reflow soldering) (lead-free solder) (modification) (organic acid)

1. Introduction

In surface mount technology, the deterioration of the wettability to the Cu pad and the electrode of the part of the solder paste according to the abolition of the use of Pb have been pointed out [1, 2]. The deterioration of the wettability influences the reliability of products with solder joints. Therefore, the improvement of the wettability is a very important technology in the electronic industry. In this research, the verification of the effect to the wettability was attempted by using the surface modification method with an organic acid from which the effect of decreasing the solid-state bonding temperature of Sn and Cu was confirmed [3]. The organic acids used in the experiment are formic acid and citric acid. For the comparison, the surface which had been processed by the procedure of making to cleanness on the Cu surface used for wettability evaluation method of the solder paste (JIS Z3284) was examined.

2. Experimental details

The sample used for the evaluation cut a fragment (3x3 mm^2) and a substrate (5x5mm^2) from the copper sheet of 1 mm in thickness. The surface to be soldered was ground on emery paper (#800). The surface modification processing was performed by boiling the Cu surface in organic acid (formic acid or citric acid). The Sn-3.0Ag-0.5Cu (mass%) solder paste was printed on the substrate by using the metal mask (120 μm in thickness) shown in **Fig. 1**. The reflow process used the heat pattern shown in **Fig. 2**. The wettability was evaluated by measuring a descent speed of the fragment in reflow process with a laser displacement meter.

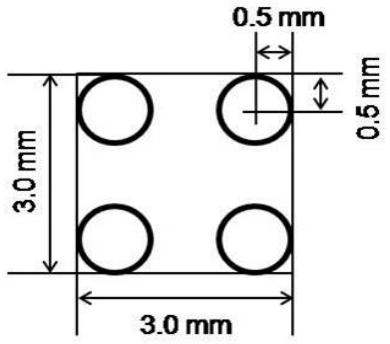

Fig. 1 Shape of metal mask used in this research.

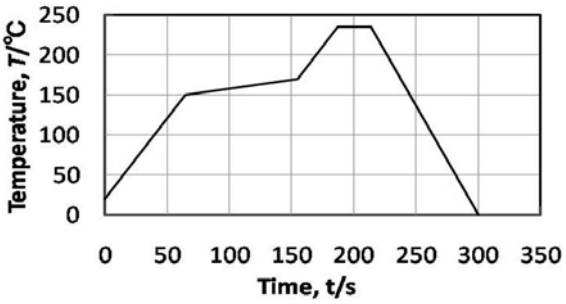

Fig. 2 Diagram of heat pattern in reflow process.

3. Results and discussion

The result of measuring descent behavior and a temperature of the fragment in the reflow process is shown in **Figs. 3-6**. A black-solid line in the figure is an average displacement curve of five examinations. As a result of the measurement, it has been understood that the fragment begins descending when the temperature of solder paste reaches the melting point, and the descent speed has approached zero with the passage of the processing time. This descent behavior showed a similar tendency regardless of the type of surface modification.

However, in the case of the fragment modified by the formic acid, it has been understood that the fragment descent speed quickens (refer to Figs. 3 and 5). When citric acid was used for the modification process, a similar effect was observed. Therefore, it was suggested that the wettability of the solder paste was improved by giving the modification process on the Cu surface with an organic acid.

To clarify the improvement mechanism for the wettability of the solder paste, the Cu surface modified by formic acid was analyzed by X-ray diffraction analysis. As a result, as shown in **Fig. 7**, Cu(II) formate was formed on the surface layer when the modification process was applied.

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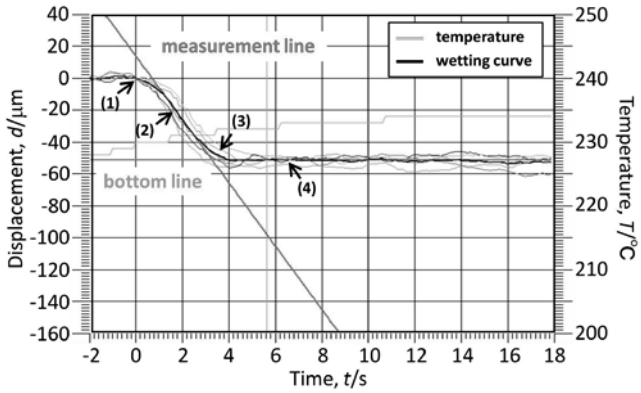

Fig. 3 Relation between descent behavior and reflow temperature (as grinding).

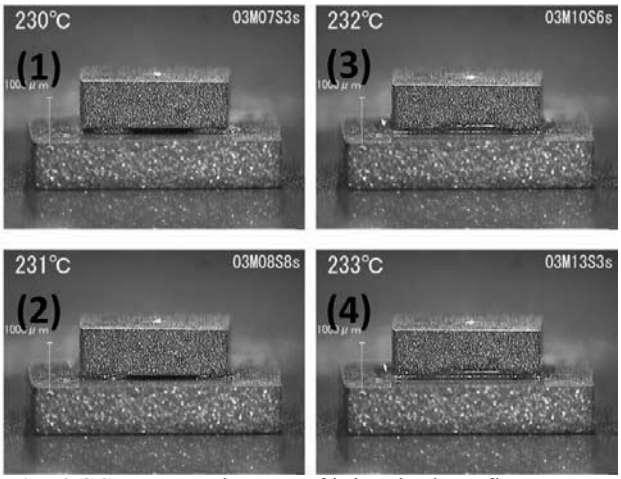

Fig. 4 CCD camera images of joints in the reflow process. The numbers in the figure correspond to those in Fig. 3.

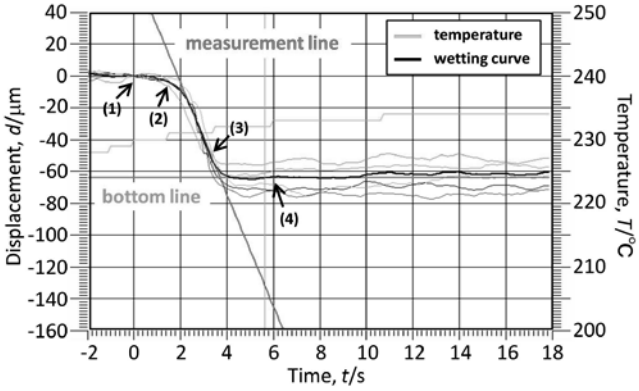

Fig. 5 Relation between descent behavior and reflow temperature (modificated by formic acid).

The generation process of Cu(II) formate is shown in following reaction formulae [4]:

$$Cu + 2HCOOH \rightarrow Cu(HCOO)_2 + H_2\uparrow \quad (1)$$
$$CuO + 2HCOOH \rightarrow Cu(HCOO)_2 + H_2O\uparrow \quad (2)$$
$$CuO_2 + 2HCOOH \rightarrow Cu(HCOO)_2 + H_2\uparrow + O_2\uparrow \quad (3)$$

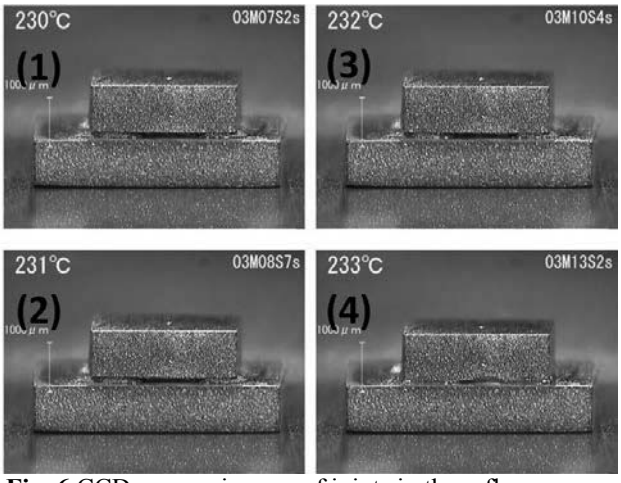

Fig. 6 CCD camera images of joints in the reflow process. The numbers in figure correspond those in Fig. 5.

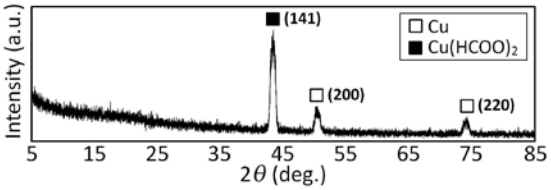

Fig. 7 X-ray diffraction patterns of surface of copper modified by formic acid.

In addition, it is known that Cu(II) formate undergoes an exothermic decomposition reaction at about 413 K, as shown by following reaction formula, and metallic copper is generated [5]:

$$Cu(HCOO)_2 \rightarrow Cu + H_2 + 2CO_2 \quad (4)$$

Therefore, it is thought that the wettability of the solder paste has been improved by surface modification process because Cu(II) formate formed on the Cu surface by modification process and metallic copper was exposed by thermal decomposition of Cu(II) formate in the reflow process. Moreover, it is thought that the wettability of the solder paste is improved in the case of the citric acid by a similar improvement mechanism. The result of obtained in this research is collectively shown in **Table 1**.

Table 1 Effect of surface modification on descent behavior.

	descent speed (μm/s)	descent amount (μm)
as grinding	20	51.3
citric acid	37	81.3
formic acid	35	64.1
JIS	25	65.1

4. Conclusions

The conclusions of this study are summarized as follows.

(1) The difference of the wettability of the solder paste which depends on the surface modification of Cu is revealed by the measurement of the descent speed of a Cu fragment with a laser displacement meter.
(2) The wettability of the solder paste to the Cu surface is rapidly improved by a surface modification process which uses an organic acid.

References

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