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The Electrical Property of Copper and Copper Alloy Particles Containing Electrically Conductive Adhesives †

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Abstract

The properties of electrically conductive adhesives filled with copper fillers containing trace elements such as Ag, Ge, Mg and Zn were investigated in terms of electrical conductivity and thermal stability. The metallic fillers were characterized by using particle size analysis and scanning electron microscopy. Oxidation of metallic fillers under high temperature exposure led to degradation of electrical conductivity in the conductive adhesives. The addition of Ag and Mg in the copper fillers had significant effects on the electrical conductivity and thermal stability in the electrically conductive adhesives.

KEY WORDS: (conductive adhesive), (copper filler), (trace element), (oxidation resistance)

1. Introduction

As the electronic packaging requirements are driven towards smaller size, higher density, and lower cost solutions, interconnections between surface mount device components and a substrate using electrically conductive adhesives (ECAs) are well positioned to meet these challenges. For many years, tin-lead solders have been widely used as joining materials in the electronics industry. However, due to the toxicity of lead in the environment and health concerns, many companies in Japan have controlled the use of lead in all their new electronic products because of the pressure to eliminate or minimize the use of harmful materials in electronic products. Therefore, lead-free solders and ECAs have been considered as the most promising alternatives to tin-lead solders for interconnections. Conductive adhesives provide a number of advantages from the standpoint of environmental impact and performance characteristics. They offer lower processing temperature, finer pitch, and better thermo-mechanical performance [1, 2]. However, current ECAs still have some limitations in terms of their electrical, thermal, and reliability properties, compared with those of tin-lead or lead-free solders, for solder replacement purpose.

ECAs are usually composed of conductive metal fillers and polymer resin. Various conductive fillers such as Ag, Ni, Cu and Pd are applied to create conductive adhesives [3-10]. Silver flakes and spherical particles are the most commonly used metallic fillers for conductive adhesives, but have the disadvantage of being relatively expensive. Therefore, alternative materials such as copper and nickel are used as the metallic fillers to manufacture low cost conductive adhesive. Cu can be a promising candidate for conductive metallic filler owing to its low resistivity, low cost and improved electro-migration performance. However, it is susceptible to oxidation which will reduce the electrical properties of the composite as a result of the nonconductive nature of such oxide layers [11]. Cu is readily oxidized at a low temperature, and has no self-protective layer to prevent further oxidation [12-14]. Therefore, the study of Cu oxidation and the development of techniques to prevent copper oxidation are crucial to the application of electrically conductive Cu fillers. In order to overcome the problem associated with the oxidation of Cu, Ag coated Cu powders have been used as metallic fillers and the effect of oxidation of these materials in conductive adhesives have been investigated [15-17]. H. K. Liou et al. [18] have found that the formation of GeO_2 on the surface oxide layer would protect Cu from oxidation. In addition, it has been demonstrated that adding small amounts of Mg to Cu can eliminate the poor corrosion resistance, increase electromigration resistance and improve electrical behavior [19, 20].

In this study, we have investigated the electrical and thermal property of the conductive adhesive containing Cu and Cu alloy fillers. The purpose of this study is to develop an ECA filled with Cu alloy fillers which is cost effective with low bulk resistivity and high thermal stability.

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2. Experimental

2.1 Materials

In this study, a total of five types of metallic fillers were prepared, i.e. pure Cu particles and four types of Cu alloy particles with Ag, Ge, Mg and Zn added as trace element, respectively, as shown in **Table 1**. The nominal amount of each trace element is prepared at 0.5 at. % and the mean diameter of the particles is about 40 μm. The diameter of the particles were determined by the laser light scattering method using a particle size analyzer (Model: SALD-7000) from Shimadzu. By using these Cu and Cu alloy particles, five types of ECAs filled with these metallic fillers at 80 wt. % were prepared. **Table 2** shows the contents of the ECAs in this study.

2.2 Methods

In order to investigate and evaluate the electrical properties of the pure Cu and Cu alloy particles in this study, an apparatus is prepared as shown in **Fig. 1** to measure the electrical conductivity of the particles. At the top, there is a motor which can be used to control the descending speed of the upper part of the Cu electrode, and the bottom part is equipped with a sensor which can sense the loading of the electrode and particles. In addition, a maximum loading of 500 N is set so that the sensor will automatically stop when it reach the maximum loading.

The experimental procedure involves by first inserting a Cu electrode into an acrylic tube with an inner diameter of 4.8 mm. Then, metallic filler is filled from the open end of the tube, and it is tapped continuously until the metallic filler reaches 1 cm. This is followed by inserting the other Cu electrode into the tube and installing it in the apparatus. A current of 10 μA is passed through the Cu electrodes from an electrical source. At this time, the voltage between the Cu electrodes is measured and the electrical resistance of the metallic fillers inside the acrylic tube calculated.

Table 1: The metallic fillers evaluated in this study

Metallic Fillers	Trace Element	Content (at. %)	Median Diameter (μm)
a	-	-	35.8
b	Ag	0.46	40.9
c	Ge	0.49	40.7
d	Mg	0.63	44.3
e	Zn	0.45	48.1

Table 2: Content of electrical conductive adhesives prepared in this study

Conductive adhesives	Metallic Fillers	Fillers content (mass %)	Phenolic resin content (mass %)
A	a	80	20
B	b	80	20
C	c	80	20
D	d	80	20
E	e	80	20

In order to investigate the relationship between the change of the loading on the metallic fillers and the electrical resistance, the voltage between the electrodes and the loading are recorded simultaneously.

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In addition to the effects of trace element on Cu fillers of the ECAs in terms of electrical conductivity and long term reliability were studied by measuring the electrical resistance of the ECA.

Fig. 2 shows the schematic diagram of the ECA samples for electrical resistance measurement. FR4 board with copper pads at both ends was used to measure the electrical resistivity of the ECA. Two parallel strips of cellophane tape were placed apart along the length of a standard 50 x 95 mm. Then, another two strips of the tape

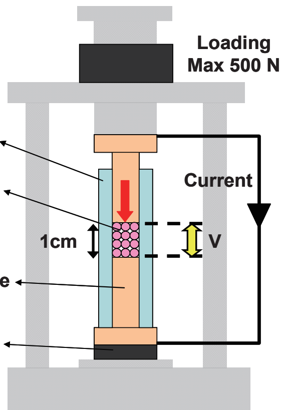

Fig. 1: Schematic diagram of apparatus for measurement of electrical resistance of metallic fillers.

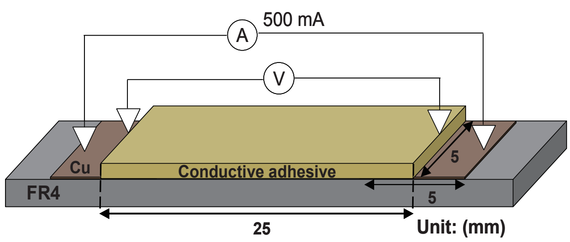

Fig. 2: Schematic diagram of FR4 for measurement of electrical resistance of ECA.

were placed perpendicular to the parallel strips in order to create a test sample with 25 mm length and 5 mm width. Using a clean stainless steel spatula, the adhesive was spread on to the space between the tape strips. The spatula is rested on the tape to provide a uniform thin application of ECA. A total of 5 test samples were prepared on a single FR4 board. After that, all the tapes were removed and the FR4 board with the ECA is placed in a convection oven to cure at 175ºC for 1h. The samples were removed from the oven after curing and allowed to cool to room temperature before the resistivity measurement. The samples were then subjected to high temperature exposure at 125ºC up to 1000 h in air to study the thermal stability of the ECA.

The resistance of the ECA was measured from ends of the pattern using a Nanovoltmeter (Model: 2182A) and Precision Current Source (Model: 6220) from Keithley, with a four-point probe. In addition, the thickness of the cured ECA samples on the FR4 board was measured by using a CCD laser displacement sensor (Model: LK-G Series) from Keyence together with software MAP-3D from COMS.

3. Results

3.1 Evaluation of electrical conductivity of metallic fillers

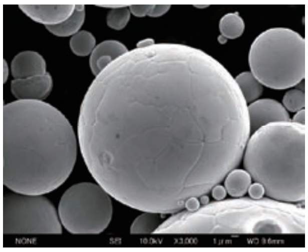

Fig.3 (i): SEM image of metallic filler a

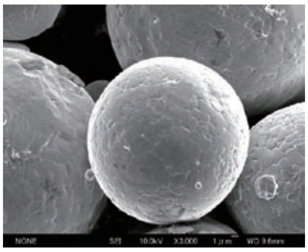

Fig. 3 (ii): SEM image of metallic filler b

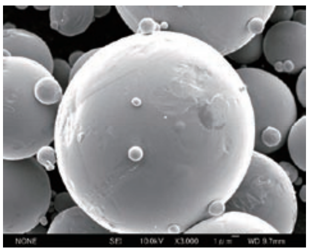

Fig. 3 (iii): SEM image of metallic filler c

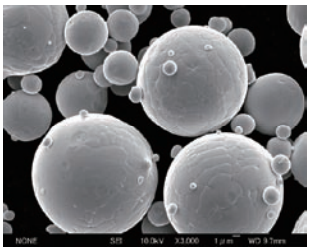

Fig. 3 (iv): SEM image of metallic filler d

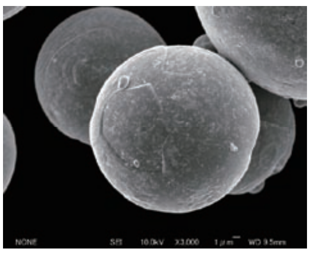

Fig. 3 (v): SEM image of metallic filler e

Fig. 3 (a), **Fig. 3 (b)**, **Fig. 3 (c)**, **Fig. 3 (d)** and **Fig. 3 (e)** reveal the SEM images of Cu, Cu - Ag, Cu - Ge, Cu - Mg and Cu - Zn particles in this study. All metallic fillers showed similar morphology with uniform spherical shapes of different sizes. **Fig. 4** depicts the particle size distribution (PSD) of the pure Cu filler, and similar results were observed in the Cu alloy fillers too. The median particle size of the fillers ranged from 36 - 48 μm as shown in Table 1. To evaluate the electrical properties of the metallic fillers in the form of powder, the apparatus illustrated in Fig. 2 was prepared to measure the electrical resistance of the metallic fillers. **Fig. 5** displays the change of electrical resistance and loading over time during typical measurement. Change of the loading and the resistance value between the electrodes could be observed clearly from the beginning of the measurement. Although the resistance is very high at the beginning of the measurement, it starts to decrease drastically when the loading reaches a certain level. Since it is difficult to compare the difference between Cu and Cu alloy fillers from the measurement curves, the electrical resistances during loading at 10 N and 500 N were extracted respectively from the graphs and presented in **Fig. 6 (a)** and **Fig. 6 (b)**.

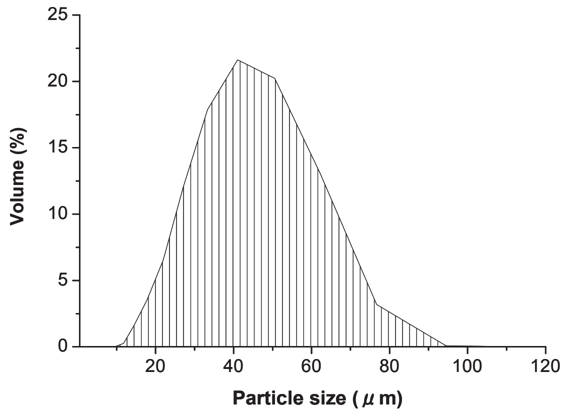

Fig. 4: Particle distribution (PSD) of metallic filler Cu

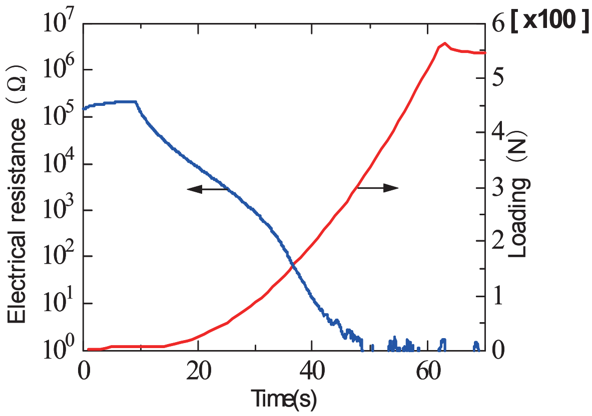

Fig. 5: Effect of loading on electrical resistance of metallic fillers over time

During loading at 10 N, the difference of electrical resistance is apparent, especially in the case with the additives Ag and Zn, a large difference of resistance could be observed compared to that of the pure Cu. However, in the case at 500 N loading, similar resistance could be found in each Cu and Cu alloy filler. Hence, it could be considered that the resistance value is reflected by the surface condition of the particles when the loading is small. However, when the loading is large, the particles are strongly pressed and the oxide layers at the surface of the particles will be broken, which would then lead to similar resistance values.

3.2 Evaluation of electrical properties of electrically conductive adhesives

To investigate the electrical conductivity and long term reliability of the electrically conductive adhesives, ECAs with pure Cu and Cu alloy fillers were prepared. The electrical resistivity of the ECAs was measured after curing at 175ºC for 1 h. **Table 3** shows the electrical resistivity of the as cured ECA. It was observed that the electrical resistivity of all the ECA is in the same order except ECA C. A substantially low electrical resistivity was observed in ECA B in which the electrical resistivity is 3.5 times lower than that of the ECA A. Vice versa, the highest electrical resistivity was observed in ECA C which is 1.5 times higher than that of ECA A. This phenomenon indicates that by adding 0.5 at. % of trace element to the pure Cu particles, the surface property of the particles will be changed and affect the electrical conductivity of the ECA.

For evaluation of long term reliability of the electrical conductivity of the ECAs, the change of electrical resistivity during high temperature exposure is shown in **Fig. 7**. The aging temperature is maintained at 398 K up to 1000 h. The resistivity of ECA A and C increased rapidly during the first 100 h of high temperature exposure. This may be attributed to the severe oxidation at the surface of the metallic fillers which leads to increased resistivity in the ECAs.

On the other hand, the electrical resistivity of ECA B and D remained low and stable throughout 1000 h under high temperature exposure. This indicates that adding Ag and Mg respectively into the Cu fillers has suppressed the oxidation of the particles and leads to stable electrical conductivity during aging. However, the mechanism of this phenomenon is not clear at the moment and needs further investigation.

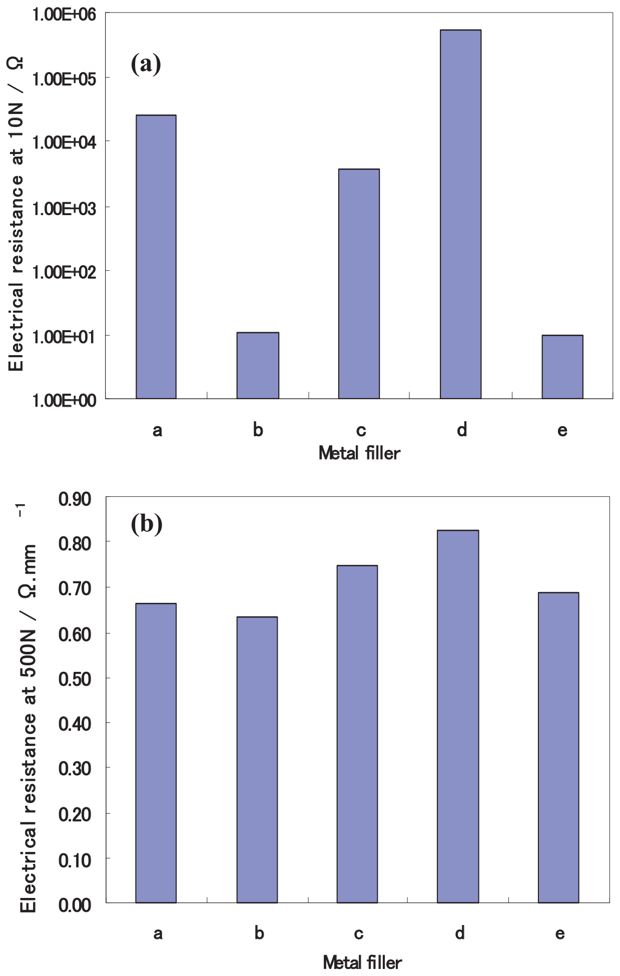

Fig. 6: Electrical resistance of the metallic fillers during loading at **(a)** 10 N, **(b)** 500 N

Table 3: The electrical resistivity of the electrically conductive adhesives after curing

Conductive Adhesives	Electrical Resistivity (10^{-4} Ω .cm)
A	8.48
B	2.38
C	12.5
D	4.53
E	8.01

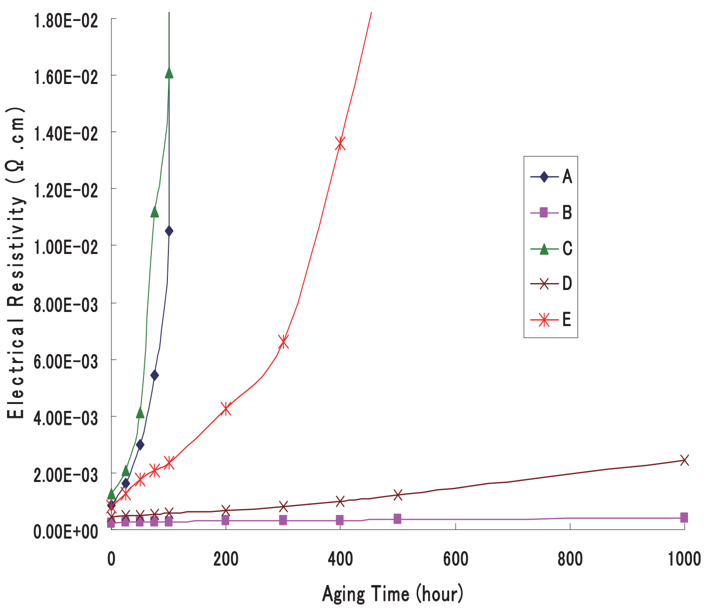

Fig. 7: The change of electrical resistivity of each ECA during high temperature exposure.

4. Conclusion

In this study, different Cu alloy particles were prepared to prevent oxidation of Cu particles which were used as the metallic fillers in ECA. The effect of trace elements on the electrical conductivity of ECA was evaluated. From the results, it was significant that the electrical resistivity of ECAs with Cu-Ag and Cu-Mg as fillers during high temperature exposure was substantially lower and the suppression of oxidation was considered to be the main factor contributing to this phenomenon.

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