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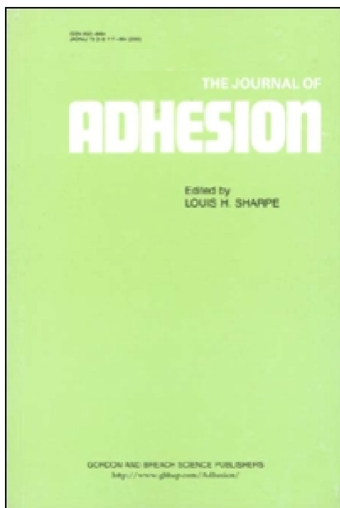

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Electrical Properties of Pre-Alloyed Cu-P Containing Electrically Conductive Adhesive

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In this study, a pre-alloyed Cu-P powder with a trace amount of P (0.002 at.%) was used as a metallic filler in a phenolic resin-based electrically conductive adhesive (ECA). The electrical property of the Cu-P-filled ECA was investigated for long-term stability and reliability by aging at high temperature exposure at 125°C and 85°C/85% RH for 1000 h, respectively. Results showed that the electrical resistivity of the Cu-P-filled ECA could be maintained consistently low after high temperature exposure at 125°C for 1000 h or aging at 85°C/85% RH for 1000 h, compared with the rapidly increased resistivity of Cu-filled ECA over time. A significantly low final resistivity at an order of magnitude of $10^{-4}\,\Omega \cdot cm$ cm could be maintained in Cu-P-filled ECA even after aging at 85°C/85% RH for 1000 h.

Keywords: Aging; Copper and alloy; Electrical properties; Phenolic

1. INTRODUCTION

Recently, electrically conductive adhesives (ECAs) have attracted increasing attention in the electronics industry as they provide a promising alternative to the conventional tin/lead solders. ECAs are believed to be more environmentally friendly with several advantages such as lower processing temperature, finer pitch capability, simpler

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process, and higher flexibility. Metal particles such as silver (Ag), nickel (Ni), and copper (Cu) have been employed as conductive fillers [1–3]. Ag is the most commonly used metallic filler in ECAs due to its low electrical resistivity, but its disadvantage is that it is relatively expensive. Cu can be a promising candidate for a conductive metallic filler owing to its low resistivity, low cost, and improved electromigration performance. However, Cu is easily oxidized in air which then leads to loss of electrical conductivity. Therefore, development of techniques to prevent copper oxidation is crucial to the application of electrically conductive Cu fillers in the ECAs. Cu-based alloys are widely used in various fields owing to their excellent electrical and thermal conductivity together with outstanding resistance to corrosion and fatigue [4,5].

In our previous study, trace elements such as Ag, Ge, Mg, and Zn were added into the Cu to prepare Cu alloy fillers for application in ECAs [6]. The results showed that addition of 0.5 at.% of Ag and Mg to the Cu fillers led to consistent electrical conductivity during high temperature exposure at 125°C for 1000 h. It has been reported that a Cu-1.11%, Mn-0.28% P alloy exhibited good electrical conductivity (51% International Annealed Copper Standard) (IACS) [7]. In this study, a trace amount of P is added in the form of pre-alloyed Cu-P to act as an anti-oxidation agent. This Cu-P powder was used as a metallic conductive filler in the ECA and the electrical property, thermal stability, and reliability of the ECA were studied.

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2. EXPERIMENTAL

2.1. Materials

2.1.1. Fabrication of Cu and Cu-P Fillers

Cu and Cu-P fillers (0.002 at.% of P) used in this study were prepared by using gas and water atomization method, respectively, by Mitsui Mining & Smelting Co. Ltd., Tokyo, Japan.

2.1.2. Fabrication of Electrically Conductive Adhesives

A phenolic resol-type resin (HR-CPTH, Harima Chemical Co., Tsukuba, Ibaraki, Japan) was used as a polymer matrix. The mass fraction of the metallic filler was 80 wt% in each ECA. The Cu and Cu-P filler were incorporated into the thermosetting resin as the adhesive matrix by mixing in an agate mortar. It was then defoamed in a hybrid defoaming mixer (Model ARE250, Thinky Corp., Osaka, Japan).

2.2. Characterization of Metallic Fillers

The morphology of each metallic filler was observed by using field emission scanning electron microscopy (Model: JSM-6500 F, JEOL Ltd., Tokyo, Japan). In addition, powder X-ray diffraction (XRD) of the metallic fillers was performed on a standard instrument JDX-3530 M from JEOL Ltd., Tokyo, Japan. The samples were measured at 2θ from 10° to 100° at a scanning speed of 2°/min.

2.3. Preparation of Samples for Electrical Resistivity Measurement

An epoxy-E-glass electrical laminate, flame retardant 4 (FR4) board (Oki Printed Circuits Co., Ltd., Niigata, Japan), with copper pads at both ends, was used to measure the electrical resistivity of ECA. Two parallel strips of cellophane tape were placed apart along the length of a standard 50×95 mm piece of FR4. Then, another two strips of the tape were placed perpendicular to the parallel strips in order to create a test specimen opening with 25-mm length and 5-mm width (as shown in Fig. 1). The adhesive was then spread in the specimen opening to create a uniform thin application of ECA. A total of five specimens were prepared on a single FR4 board for each sample. All the tapes were then removed and the FR4 board with ECAs was put into a convection oven for curing at 175°C for 1 h. The samples were removed from the oven after curing and were allowed to cool to room temperature before the resistivity measurement. The samples were then subjected to high temperature exposure at 125°C for up to 1000 h in air to study the thermal stability of the ECA. Another set of

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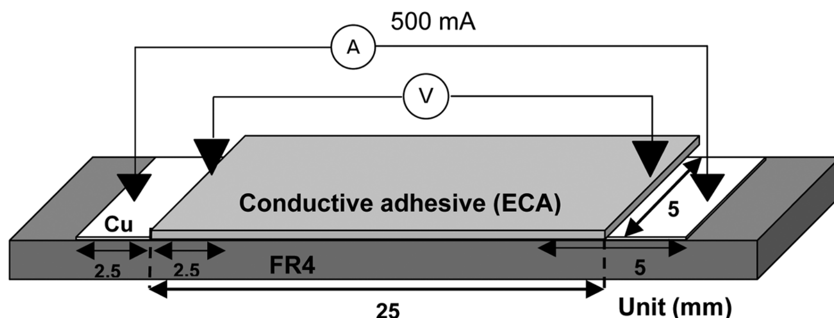

FIGURE 1 Schematic diagram of FR4 for measurement of electrical resistance of ECA.

samples were aged under 85°C/85% RH conditions for 1000 h in a temperature and high-humidity chamber (Model: SC01 Junior, ETAC, Tokyo, Japan). The resistance of the ECA was measured using a nanovoltmeter (Model: 2182A, Keithley Instruments, Tokyo, Japan) and precision current source (Model: 6220, Keithley Instruments, Tokyo, Japan) by a four-point probe method. The thicknesses of the cured ECA samples were measured using a CCD laser displacement sensor (Model: LK-G Series, Keyence Corp., Osaka, Japan) together with software MAP-3D from COMS Corp., Hyogo, Japan.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction (XRD)

Figure 2 shows the XRD patterns of the Cu and Cu-P fillers used in this study. The diffraction peaks at $2\theta = 43.30$, 50.43, and 74.13° correspond to the *fcc* structure of Cu $\cdot$ ($h\ k\ l$) (1 1 1), (2 0 0), and (2 2 0) planes could be observed in both Cu and Cu-P fillers. Due to the trace amount of P (0.002 at.%) in the sample, only Cu diffraction peaks could be observed in the Cu-P filler.

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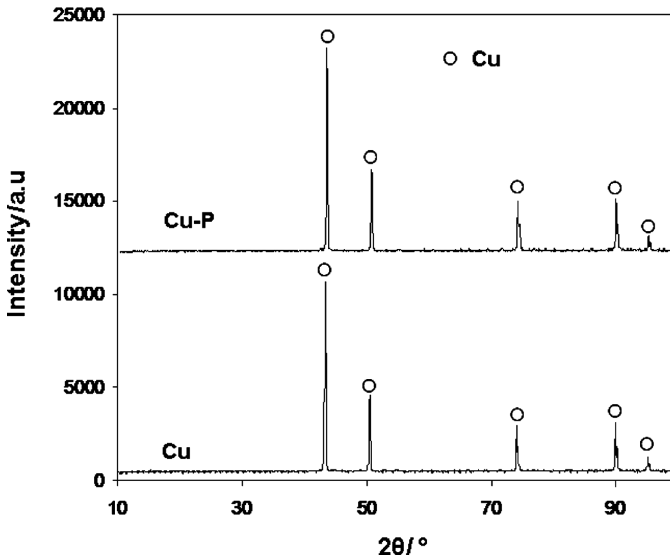

FIGURE 2 XRD patterns of the Cu and Cu-P fillers used in this study.

3.2. Morphology of Metallic Fillers

Figure 3(a) depicts the SEM image of Cu filler which reveals that the sample is mostly composed of uniform spherical particles within the range of 1.3–38 μm. However, the SEM image of Cu-P filler [Fig. 3(b)] shows that besides some spherical particles (1.4–30 μm), most of the particles possess an irregular shape.

3.3. High Temperature Exposure

The thermal stability of ECAs prepared in this study was investigated under high temperature exposure at 125°C for 1000 h. Figure 4 depicts the change of resistivity of ECAs during aging. It is significant that the Cu-filled ECA lost its electrical conductivity when the resistivity increased drastically during the first 100 h of aging. However, the resistivity of Cu-P-filled ECA remained consistently low over 1000 h. This indicates that the ECA filled with Cu-P is thermally stable compared with the Cu-filled ECA that could not withstand the high temperature exposure at 125°C for 1000 h. The loss of electrical conductivity in the Cu-filled ECA could be attributed to the oxidation of the Cu fillers inside the ECA. Figure 5 shows the SEM image and EDX result of the Cu-filled ECA after high temperature exposure at 125°C for 400 h. It is significant that the surface of the Cu filler has become porous due to oxidation of Cu. It has also been reported by Haugsrud [8] that the oxide scales contained a considerable amount of porosity. The EDX result (inset of Fig. 5) also showed the presence of oxide on the surface of the Cu filler.

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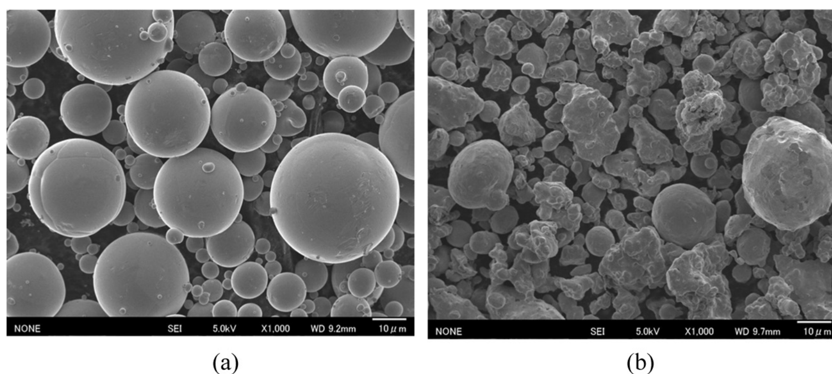

FIGURE 3 (a) SEM image of Cu filler and (b) SEM image of Cu-P filler.

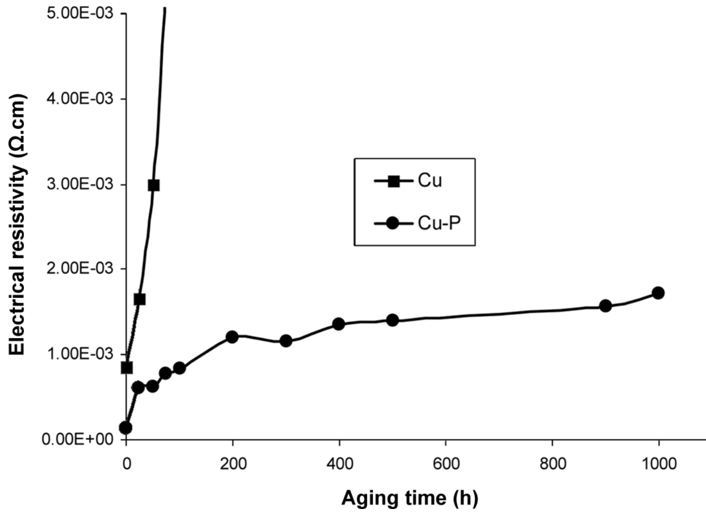

FIGURE 4 Resistivity of Cu- and Cu-P-filled ECAs during high temperature exposure at 125°C over 1000 h.

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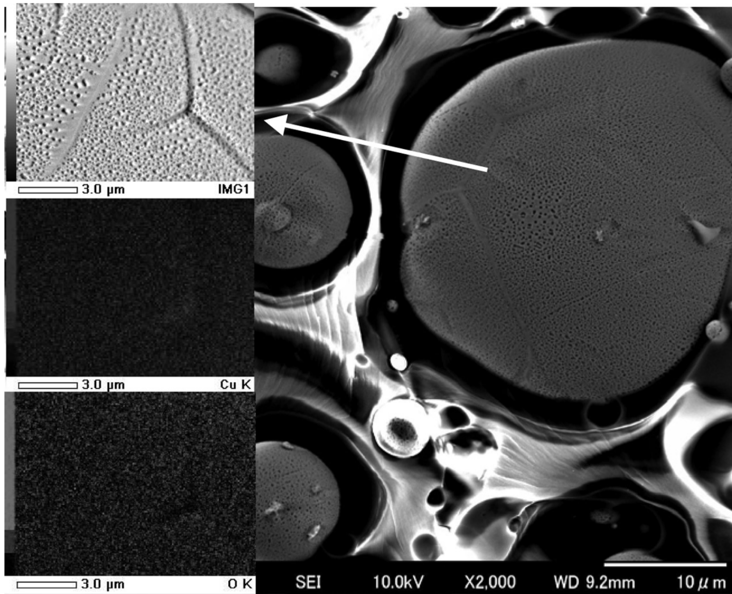

FIGURE 5 SEM image and EDX result of the Cu-filled ECA after aging at 125°C for 400 h.

Figures 6(a) and 6(b) depict the SEM image of the as-cured Cu-P-filled ECA and Cu-filled ECA, respectively. Compared with the smooth and spherical surface of Cu fillers as shown in Fig. 6(a), the rough surface of Cu-P fillers may enhance the binding of the metallic filler with the polymer matrix of phenolic resin. Hence, it is found that Cu-P fillers are covered more completely with resin [Fig. 6(a)], compared with the Cu-filled ECA in which the Cu particles are largely exposed to the air at the surface of ECA as shown in Fig. 6(b). This may lead to rapid oxidation of the Cu fillers.

On the other hand, the thermal stability of the Cu-P-filled ECA could be due to the oxidation-resistant behavior of the Cu-P filler. Generally, the surface of the commercial metal powder consists of many impurities, especially the oxide layer on the surface of the particles [5]. In this case, P can act as an antioxidant. The phosphorus reacts with CuO to produce metallic Cu as one of the products of the reaction.

$$5CuO + 2P = P_2O_5 + 5Cu \quad (1)$$

At 298.15 K, the change in the Gibbs free energy (ΔG) of reaction (1) is -714.23 kJ mol. As ΔG was negative, it leads to a spontaneous reaction. This reaction prevented the metal surface from oxidation, leading to clean metal/metal interfaces [9,10]. As a result, Cu-P filler with an oxidation-preventive surface would lead to consistent electrical conductivity with low resistivity in the ECA throughout 1000 h at 125°C.

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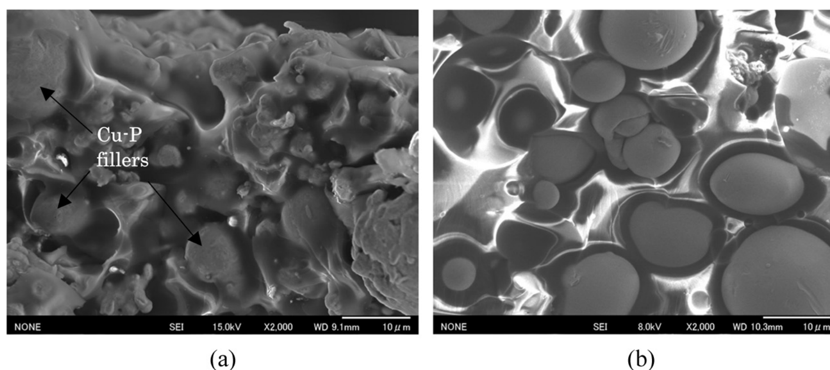

FIGURE 6 (a) SEM image of the as-cured Cu-P-filled ECA and (b) SEM image of the as-cured Cu-filled ECA.

3.4. 85°C/85% RH Aging

Figure 7 depicts the 85°C/85% RH aging of the ECAs in this study. Compared with the aging of ECAs under high temperature exposure at 125°C, a similar trend could be observed in the change of electrical resistivity of the ECAs during aging at 85°C/85% RH. The electrical resistivity of the Cu-P-filled ECA remained relatively stable and consistently low over time compared with that of the Cu-filled ECA. The Cu-P-filled ECA could withstand 1000 h aging at 85°C/85% RH without significant change in resistivity in which a final resistivity ($2.68 \times 10^{-4}\,\Omega \cdot cm$) at an order of magnitude of $10^{-4}\,\Omega \cdot cm$ could be achieved. Furthermore, the resistivity of this Cu-P-filled ECA during aging at 85°C/85% RH was relatively low and consistent over 1000 h compared with its resistivity during high temperature exposure at 125°C.

Conversely, the Cu-filled ECA showed a rapid increase in resistivity within the first 200 h of aging, although the loss of electrical conductivity was relatively slow compared with that of the high temperature exposure at 125°C. This indicates that the oxidation process proceeded more rapidly in the ECAs during high temperature exposure at 125°C compared with aging at 85°C/85% RH.

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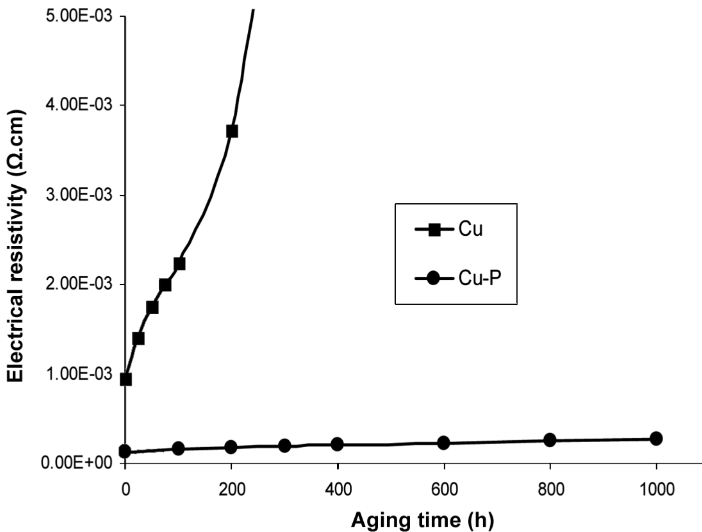

FIGURE 7 Resistivity of Cu- and Cu-P-filled ECAs during aging at 85°C/85% RH for 1000 h.

4. CONCLUSION

In summary, we can conclude that the presence of a trace amount of phosphorous (0.002 at.%) in the Cu filler is effective in preventing oxidation of Cu in the ECA. Compared with the Cu-filled ECA, the resistivity of Cu-P-filled ECA was relatively stable and low after high temperature exposure at 125°C for 1000 h or aging at 85°C/85% RH for 1000 h. The thermal stability of the Cu-P-filled ECA may due to the antioxidation behavior of P in the Cu which tends to reduce CuO to Cu in a spontaneous reaction. This prevents the metal surface from oxidizing and leads to a clean metal surface.

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REFERENCES

[1] Jeong, W. J., Nishikawa, H., Itou, D., and Takemoto, T., *Mater. Trans.* **46**, 2276–2281 (2005).
[2] Goh, C. F., Yu, H., Yong, S. S., Mhaisalkar, S. G., Boey, F. Y. C., and Teo, P. S., *Thin Solid Films* **504**, 416–420 (2006).
[3] Zhao, H. S., Liang, T. X., and Liu, B., *Inter. J. Adhesion and Adhesives* **27**, 429–433 (2007).
[4] Zhu, H. H., Lu, L., and Fuh, J. Y. H., *J. Mater. Process Tech.* **140**, 314–317 (2003).
[5] Zhu, H. H., Lu, L., Fuh, J. Y. H., and Wu, C. C., *Mater. and Design* **27**, 166–170 (2006).
[6] Ho, L. N., Nishikawa, H., Natsume, N., Takemoto, T., Miyake, K., Fujita, M., and Ota, K., *J. Elect. Mater.* **39**, 115–123 (2010).
[7] Choi, J. H., Byun, J. S., and Lee, D. N., *J. Mater. Sci.* **35**, 151–157 (2000).
[8] Haugsrud, R., *Corrosion Science* **42**, 383–399 (2000).
[9] Gu, D. D. and Shen, Y. F., *Metallurgical and Mater. Trans. B* **37B**, 967–977 (2006).
[10] Gu, D. D., Shen, Y. F., and Lu, Z. J., *Mater. and Design* **30**, 2099–2107 (2009).