



## Original Article

# A metal–metal bonding process using metallic copper nanoparticles produced by reduction of copper oxide nanoparticles

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### ABSTRACT

Metal–metal bonding was performed using metallic Cu nanoparticles fabricated from CuO nanoparticles. Colloid solutions of CuO nanoparticles were prepared by the reaction of  $\text{Cu}(\text{NO}_3)_2$  and NaOH in aqueous solution at reaction temperatures ( $T_{\text{CuO}}$ ) of 20, 40, 60 and 80 °C. CuO single crystallites with a size of ca. 10 nm were produced, and they formed leaf-like aggregates. The longitudinal and lateral sizes of the aggregates decreased from 522 to 84 nm and from 406 to 23 nm, respectively, with an increase in  $T_{\text{CuO}}$ . Colloid solutions of metallic Cu nanoparticles were prepared by reducing the CuO nanoparticles with hydrazine in the presence of cetyltrimethylammonium bromide. The size of the metallic Cu nanoparticles decreased from 92 to 73 nm with increasing  $T_{\text{CuO}}$ . Metallic copper discs were bonded with the metallic Cu nanoparticles by annealing at 400 °C and 1.2 MPa for 5 min in  $\text{H}_2$  gas. The shear strength required to separate the bonded discs increased with increasing  $T_{\text{CuO}}$ . A maximum shear strength of 39.2 MPa was recorded for a  $T_{\text{CuO}}$  of 80 °C.

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## 1. Introduction

In metal–metal bonding processes, which are important in many fields, solders or fillers have conventionally been used for efficient bonding [1–5]. These solders are melted at high temperatures and spread between metallic surfaces, thus bonding the surfaces together. A decrease in temperature solidifies the metallic materials and completes the metal–metal bonding. Metallic alloys composed mainly of lead and tin have been used as solders [1–4]. These metallic alloys

melt at temperatures as low as 184 °C, lower than the melting points of many other metallic alloys. The lead- and tin-based alloys diffuse into the materials to be bonded, and then, they can be bonded at low temperatures. It is well known that lead is harmful to living bodies, which limits its use. Various lead-free alloys have been developed as new solders [6–11]. Although low-temperature metal–metal bonding can be performed using the lead-free solders, there is a serious problem: the bonded materials may break apart when exposed to temperatures higher than their melting points due to remelting of the solders.

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Metallic materials such as Au, Ag and Cu can be used as the filler because they have excellent electrical and thermal conductivities. However, their melting points are ca. 1000 °C, higher than those of the conventional lead- and tin-based solders. High-temperature annealing is required during the bonding process to successfully bond metallic materials, and these high temperatures thermally damage the material near the bonding site.

The melting points of metallic materials such as Au, Ag and Cu are ca. 1000 °C in the bulk state but decrease as the material size is decreased to several nanometers [12–16]. This decrease in the melting point decreases the temperature needed for the metal–metal bonding process. Once the metallic materials are bonded with the metallic nanoparticles, they remain bonded even at temperatures higher than the melting points of the metallic nanoparticles because the nanoparticles convert to a bulk state during bonding. Various researchers have studied metal–metal bonding using metallic Ag nanoparticles as the filler [15,17–23] because metallic Ag is chemically stable. Although Ag nanoparticles work well as a filler for metal–metal bonding, they have some disadvantages: metallic Ag is relatively expensive and prone to migration under an applied voltage, which may damage an electric circuit.

Metallic Cu is promising as a filler for bonding because it is inexpensive and because electric migration does not take place as often as it does with metallic Ag. Several researchers have studied metal–metal bonding using metallic Cu nanoparticles [20,24,25]. Our research group has developed a method for producing metallic Cu nanoparticles for use as the filler in metal–metal bonding [26–30]. Metallic Cu nanoparticles are usually prepared using methods based on the direct reduction of copper ions with reducing reagents in the liquid phase. Copper oxide can also be used as a precursor. Previously, our research group proposed a method for fabricating metallic Cu nanoparticles using CuO nanoparticles as the precursor and examined the metallic Cu nanoparticles as a filler for bonding [31]. We also varied the morphologies of CuO nanoparticles and CuO-nanoparticle aggregates with several parameters such as the reaction temperature [32]. The morphology of metallic Cu particles depended on the morphologies of the CuO nanoparticles and CuO-nanoparticle aggregates as well as on the concentrations of chemicals. The metal–metal bonding properties are related to the morphology of the metallic Cu nanoparticles. In the present work, metallic Cu nanoparticles are fabricated from CuO nanoparticles with various preparation parameters and are examined with respect to metal–metal bonding.

## 2. Experimental work

### 2.1. Chemicals

The reactants for the production of copper oxide were copper (II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) (77.0–80.0% (as  $\text{Cu}(\text{NO}_3)_2$ )) and sodium hydroxide solution (NaOH) (5 M). Hydrazine monohydrate (>98.0%) and cetyltrimethylammonium bromide (CTAB) (99%) were used as a reducing reagent for copper oxide and as a stabilizer for the resulting metallic Cu nanoparticles, respectively. All chemicals were purchased

from Kanto Chemical Co., Inc. and were used as received. Water that was ion-exchanged and distilled with a Yamato WG-250 system was used in all preparations, and it was deaerated by bubbling with  $\text{N}_2$  gas for 30 min prior to preparation of the aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$ .

### 2.2. Preparation

Colloid solutions of copper oxide nanoparticles were synthesized using a reaction between copper ions and a base, as described in our previous work [31]. An aqueous solution of NaOH was added to an aqueous solution of  $\text{Cu}(\text{NO}_3)_2$  with vigorous stirring at reaction temperatures ( $T_{\text{CuO/S}}$ ) of 20, 40, 60 and 80 °C. The reaction times were 3 h at  $T_{\text{CuO/S}}$  of 60 and 80 °C and 24 h at  $T_{\text{CuO/S}}$  of 20 and 40 °C. The initial concentrations of  $\text{Cu}(\text{NO}_3)_2$  and NaOH were  $1.25 \times 10^{-2}$  and  $2.375 \times 10^{-2}$  M, respectively, which resulted in an Na/Cu molar ratio of 1.9 in the final solution.

Colloid solutions of metallic Cu nanoparticles were synthesized by reducing the copper oxide nanoparticles. An aqueous solution of CTAB was added to the colloid solution of copper oxide nanoparticles. After 30 min, hydrazine was added. Both the additions were performed in air with vigorous stirring at a constant solution temperature of 30 °C, and the reaction time was 3 h. Initial concentrations of Cu, hydrazine and CTAB in the final colloid solution were  $1.0 \times 10^{-2}$ , 0.8 and  $5.0 \times 10^{-3}$  M, respectively. The resulting nanoparticles were washed first with centrifugation at 10,000 rpm for 30 min, followed by the removal of the supernatant, the addition of water, and shaking of the mixture with a vortex mixer to disperse the nanoparticles. This process was performed three times. The powdered nanoparticles were obtained by drying the nanoparticles at room temperature in a vacuum after the final removal of the supernatant.

### 2.3. Characterization

The particles were characterized by transmission electron microscopy (TEM) and X-ray diffractometry (XRD). TEM observation was performed with a JEOL JEM-2100 microscope operating at 200 kV. Samples for TEM were prepared by dropping and evaporating the nanoparticle colloid solution on a collodion-coated copper grid. Dozens of particle diameters were measured in TEM images to determine an average particle size and a standard deviation. XRD patterns were obtained with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA with  $\text{Cu K}\alpha_1$  radiation. Samples for XRD were prepared by removing the supernatant of the nanoparticle colloid solution with decantation and drying the residue at room temperature for 24 h in a vacuum.

The metal–metal bonding properties of metallic Cu nanoparticles were investigated by a method described in our previous work [21,33–35]. The powdered particles, which were prepared using the same process as that used for the XRD samples, was spread on a copper stage with a diameter of 10 mm and a thickness of 5 mm. A copper plate with a diameter of 5 mm and a thickness of 2.5 mm was placed on top of the powder sample. The copper stage and plate were pressed at 1.2 MPa while annealing in  $\text{H}_2$  at 400 °C for 5 min with a Shinko Seiki vacuum reflow system. After bonding, the copper stage

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