Original Article

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

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\textbf{A B S T R A C T}

Metal–metal bonding was performed using metallic Cu nanoparticles fabricated from CuO nanoparticles. Colloid solutions of CuO nanoparticles were prepared by the reaction of Cu(NO\textsubscript{3})\textsubscript{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 H\textsubscript{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 \cite{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 \cite{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 \cite{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 (Cu(NO$_3$)$_2$·3H$_2$O) (77.0–80.0% (as Cu(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 N$_2$ gas for 30 min prior to preparation of the aqueous solutions of Cu(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 Cu(NO$_3$)$_2$ with vigorous stirring at reaction temperatures (T$_{CuO}$) of 20, 40, 60 and 80 °C. The reaction times were 3 h at T$_{CuO}$s of 60 and 80 °C and 24 h at T$_{CuO}$s of 20 and 40 °C. The initial concentrations of Cu(NO$_3$)$_2$ and NaOH were 1.25 × 10$^{-2}$ and 2.375 × 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 × 10$^{-2}$, 0.8 and 5.0 × 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 Cu K$_α$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 H$_2$ at 400 °C for 5 min with a Shinko Seiki vacuum reflow system. After bonding, the copper stage
and plate were separated by applying a shear strength, which was measured with a Seishin SS-100KP bond tester. The bonding and the measurement of shear strength were performed two or three times for each sample and averaged to determine the bonding strength of the nanoparticles. The surface of each copper plate was observed by scanning electron microscopy (SEM) with a JEOL JSM-5600LV microscope after the measurement of shear strength.

3. Results and discussion
3.1. Morphology of copper oxide nanoparticles

The blue aqueous solution of Cu(NO$_3$)$_2$ became a black colloid solution after the addition of the NaOH solution. Because CuO is black, this observation implied the production of CuO. Fig. 1 shows the TEM images of the prepared nanoparticles, of which colloid solutions were prepared at various $T_{\text{CuO}}$. At a $T_{\text{CuO}}$ of 20°C, leaf-like aggregates with an average longitudinal size of 522 nm and an average lateral size of 406 nm were produced. A high magnification image (inset of Fig. 1(a)) revealed that the aggregates appeared to be composed of nanoparticles with a size of ca. 10 nm, which is only an estimate, as the outlines of the nanoparticles were not well defined in the TEM images. The addition of NaOH made the pH of the solution approach its isoelectric point (IEP) without exceeding it because the Na/Cu ratio of 1.9 was lower than the stoichiometric ratio of 2 required for complete reaction of NaOH and Cu$^{2+}$. This increase in pH decreased the surface charge of the nanoparticles, which resulted in their aggregation. The aggregate size decreased with increasing $T_{\text{CuO}}$; the longitudinal/lateral aggregate sizes (in nm) were 522 ± 43/406 ± 39 at 20°C, 208 ± 22/151 ± 9 at 40°C, 75 ± 10/48 ± 9 at 60°C and 84 ± 15/23 ± 5 at 80°C. This trend corresponded with our previous work [32], which examined the fabrication of CuO particles at initial concentrations of 1.0 × 10$^{-2}$ M Cu(NO$_3$)$_2$ and 1.9 × 10$^{-2}$ M NaOH. In our previous work [31], the IEP of CuO particles prepared at 80°C was higher than that of CuO nanoparticles prepared at 20°C. Therefore, at a $T_{\text{CuO}}$ of 80°C, the pH did not closely approach the IEP. Consequently, electrostatic repulsions between the nanoparticles limited aggregation, and small aggregates were produced at high $T_{\text{CuO}}$.

Fig. 2 shows the XRD patterns of the CuO nanoparticles. For the particles prepared at 20°C, the dominant peaks were at 12.8° and 25.8°. These peaks were assigned to Cu$_2$(OH)$_3$NO$_3$ (JCPDS card No. 15-0014). In addition, several peaks attributed to monoclinic CuO (JCPDS card No. 5-0661) were recorded at 35.6°, 38.8°, and 48.9°. The appearance of Cu$_2$(OH)$_3$NO$_3$ peaks indicated that the $T_{\text{CuO}}$ of 20°C was too low for complete reaction of Cu(NO$_3$)$_2$ to CuO. At $T_{\text{CuO}}$ over 20°C, the Cu$_2$(OH)$_3$NO$_3$ peaks disappeared, and only the peaks due to CuO were detected. Accordingly, it was found that the purity of CuO nanoparticles increased with increasing $T_{\text{CuO}}$. Application of the Scherrer equation to the XRD line broadening of the 35.6° peak provided average CuO crystal sizes of 12.6, 14.3, 13.4 and 10.7 nm for 20, 40, 60 and 80°C, respectively. There

![Fig. 1](image_url) – TEM images of various nanoparticles. Colloid solutions of samples (a)–(d) were prepared with the salt–base reaction at 20, 40, 60, and 80°C.
was no large difference in crystal size at the $T_{\text{CuO}}$ examined. These crystal sizes of ca. 10 nm were similar to the sizes of the nanoparticles composing the aggregates. This similarity indicated that single crystals of CuO formed the aggregates.

3.2. Morphology of metallic copper nanoparticles

The addition of hydrazine reddened the colloid solution of CuO nanoparticles. Since surface plasmon resonance absorption of metallic Cu nanoparticles results in a red color, the reddening implied the production of metallic Cu nanoparticles. Fig. 3 shows TEM images of the metallic Cu particles. The particles had rough surfaces. Although some particles larger than 1 μm were observed, almost all of the nanoparticles examined had sizes in the range of 50–150 nm. The average particle sizes were $92 \pm 33$, $93 \pm 33$, $101 \pm 37$ and $73 \pm 23$ nm for $T_{\text{CuO}}$ of 20, 40, 60 and 80 °C, respectively; the particle size was approximately constant in the $T_{\text{CuO}}$ range of 20–60 °C but decreased when the $T_{\text{CuO}}$ was increased to 80 °C. As shown in Fig. 1, the aggregate size decreased with increasing $T_{\text{CuO}}$. Accordingly, aggregate size was considered a reflection of particle size.

Fig. 4 shows the XRD patterns of the metallic Cu nanoparticles. The patterns showed peaks at 43.3°, 50.3° and 74.2°. These peaks were attributed to cubic metallic Cu (JCPDS card No. 4-0836). In addition to the metallic Cu peaks, a faint peak was detected at 36.6° in each pattern. This peak was assigned to cubic metallic Cu$_2$O (JCPDS card No. 5-0667). The detection of Cu$_2$O indicated that the nanoparticles were partially oxidized. The average crystal sizes of the metallic Cu nanoparticles,
which were estimated from the XRD line broadening of the 43.3° peak using the Scherrer equation, were 33.1, 31.1, 28.2 and 32.6 nm at $T_{\text{CuO}}$s of 20, 40, 60 and 80 °C, respectively. The particle size observed with TEM was larger than the crystal size, which indicated that the nanoparticles were polycrystalline.

3.3. Bonding properties of metallic copper nanoparticles

Fig. 5 shows the photographs of the copper plates after the measurement of shear strength. For all the particles examined, the pressed powders on the plates appeared to be faintly reddish due to the presence of metallic Cu: the powders were still metallic after the bonding process. This observation implies that the metallic Cu powders strongly bonded the copper discs together.

Fig. 6 shows shear strength as a function of $T_{\text{CuO}}$. All of the shear strengths measured were over 20 MPa, which indicated that the copper discs were strongly bonded for all the particles examined and also corresponded to the strong bonding implied in Fig. 5. The shear strength increased with increasing $T_{\text{CuO}}$ and reached 39.2 MPa at a $T_{\text{CuO}}$ of 80 °C, which was the largest in the present work. As shown in Fig. 3, the particle size decreased with increasing $T_{\text{CuO}}$. Small particles have a larger surface area than large particles if the amount of material is the same. Therefore, the contact area between the particles and the Cu discs was larger for the small particles, as a result of the larger surface area, than for the large particles. This large contact area for the small particles probably caused the strong metal–metal bonding. There are other possible causes as well. One possible cause involves impurities in the metallic Cu nanoparticles. Our previous work showed...
that the presence of Cu₂(OH)₃NO₃ decreased the bonding ability [31]: during bonding, the elimination of NO₃ and H₂O from Cu₂(OH)₃NO₃ produced pores that prevented the particles from sintering, thus decreasing the shear strength. In the present work, the CuO nanoparticles fabricated at the low T_{CuO} contained Cu₂(OH)₃NO₃, while the purity of CuO nanoparticles increased with increasing T_{CuO}, as indicated by the XRD measurements (Fig. 2). Because the CuO nanoparticles were the precursor of the metallic Cu particles, the purity of the metallic Cu nanoparticles should depend on that of the CuO nanoparticles. The purity of the metallic Cu nanoparticles might increase with increasing T_{CuO}, while Cu₂(OH)₃NO₃ might remain in the metallic Cu nanoparticles derived from the CuO nanoparticles produced at the low T_{CuO}. Therefore, the metallic Cu nanoparticles derived from the CuO nanoparticles produced at the high T_{CuO} probably did not contain much Cu₂(OH)₃NO₃, and elimination of NO₃ and H₂O did not occur during bonding in the metallic Cu nanoparticles at high T_{CuO}. Thus, no decrease in bonding ability as a result of impurities was expected for the high T_{CuO} sample. The other possible cause of strong metal–metal bonding in the high T_{CuO} sample involves a size effect. Sintering of particles takes place intensively for small particles because of the size effect related to the depression of the melting point. This intensive sintering might have contributed to the strong metal–metal bonding with high T_{CuO}, at which the smaller nanoparticles were produced. These three factors are the possible mechanisms for the strong bonding achieved by the nanoparticles fabricated at the T_{CuO} of 80 °C.

Fig. 7 shows the SEM images of the surfaces of the copper discs separated with shear stress. Some dimples accompanied by sharp tips were observed on the surfaces for the samples at T_{CuO}s of 20 and 80 °C. When the metallic materials are separated with shear stress, dimples often form in the bonded

**Fig. 6** – Shear strength vs. T_{CuO}. The powders used were the metallic Cu particles (a)–(d) shown in Fig. 3.

**Fig. 7** – SEM images of the copper plates after the measurement of shear strength. The powders used were the metallic Cu particles (a)–(d) shown in Fig. 3.
region. Such dimples were produced in materials that underwent a strong bonding process using Ag nanoparticles, as reported by Morisada et al. [20] Therefore, the observation of dimples on the copper disks suggests that they were strongly bonded using the metallic Cu nanoparticles. For the $T_{\text{CuO}}$ of 40 and 60 °C, clear dimples were not observed, but the bonded materials appeared to be sharply cut off. This sharp cut-off also indicated strong bonding.

4. Conclusions

Colloid solutions of leaf-like aggregates composed of CuO single crystallites with a size of ca. 10 nm were prepared by reacting $1.25 \times 10^{-2}$ M Cu(NO$_3$)$_2$ with NaOH in aqueous solutions at an Na/Cu ratio of 1.9 and at $T_{\text{CuO}}$ of 20, 40, 60 and 80 °C. The aggregate size decreased from 522 to 84 nm for longitudinal size and from 406 to 23 nm for lateral size with an increase in $T_{\text{CuO}}$ from 20 to 80 °C. The CuO nanoparticles, with a Cu concentration of $1.25 \times 10^{-2}$ M in the colloid solution, were reduced with 0.8 M hydrazine in the presence of 5.0 $\times$ $10^{-3}$ M CTAB in water at 30 °C to produce the metallic Cu nanoparticles. The size of the metallic Cu nanoparticles decreased from 92 to 73 nm with an increase in $T_{\text{CuO}}$ from 20 to 80 °C. The bonding strength of the particles was examined by putting the metallic Cu nanoparticles between two metallic copper discs and then annealing the discs at 400 °C at a pressure of 1.2 MPa for 5 min in H$_2$ gas. The shear strength required to separate the bonded discs increased with increasing $T_{\text{CuO}}$, reaching a maximum of 39.2 MPa at a $T_{\text{CuO}}$ of 80 °C. Further studies on the practical use of metallic Cu nanoparticles and the precise bonding mechanism are in progress.

Conflicts of interest

The authors declare no conflicts of interest.

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