Original Article

Metal–metal bonding process using cuprous oxide nanoparticles

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\textbf{ABSTRACT}

This work performs metal–metal bonding by using cuprous oxide (Cu\textsubscript{2}O) nanoparticles prepared by reduction in aqueous solution. A colloid solution of Cu\textsubscript{2}O nanoparticles was prepared by mixing Cu(NO\textsubscript{3})\textsubscript{2} aqueous solution and NaBH\textsubscript{4} aqueous solution. Cu\textsubscript{2}O nanoparticles with a size of 111 ± 34 nm, cubic crystal phase, and crystal size of 21.2 nm were produced at initial concentrations of 0.010 M Cu(NO\textsubscript{3})\textsubscript{2} and 0.010 M NaBH\textsubscript{4} at a temperature of 40°C. The Cu\textsubscript{2}O particles contained not only Cu—O bonds but also Cu\textsuperscript{2+}—Cu\textsuperscript{2+} bonds, which indicated formation of fine cluster-like domains composed of Cu\textsuperscript{2+}—Cu\textsuperscript{2+} bonds. The shear strength required for separating the metallic Cu discs bonded by using the particles as a filler at 400°C in H\textsubscript{2} gas was as high as 27.9 MPa, which was comparable to the shear strengths of metallic Cu particles and CuO particles reported in our previous works. Metallic Cu single crystallites were produced during the bonding process. The presence of the fine cluster-like domains promoted epitaxial particle growth of the metallic Cu and formation of the micron-sized domains composed of nano-sized and submicron-sized single crystals, which provided the strong bonding.

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1. Introduction

Metal–metal bonding is an important process in fields such as electronics, metalworking industry, structural materials, and materials science [1–4]. A process using either solder or filler is an example of the various metal–metal bonding processes that are mainly used in the field of electronics. Fillers often used in conventional solder-based bonding are metallic alloys composed mainly of lead and tin [5–7], because they have low melting points so that the bonding can be made with little energy with no thermal damage to the materials to be bonded or the joints. Since lead is harmful to living creatures [8–10], its use tends to be limited. Accordingly, lead-free alloys are desirable as fillers. Among lead-free alloys, tin-based alloys have been developed as new fillers [11–15]. However, both types of alloys have a problem due to their low melting points. If the joints are kept at temperatures higher than their melting points, the alloys remelt, which may release the joints.
The field of electronics requires fillers to be electrically and thermally conductive. Metals such as Au, Ag, and Cu are candidates for fillers because of their high electric conductivity and thermal conductivity. However, metal–metal bonding using such metallic fillers has to be performed at high temperature because their melting points are higher than those of the conventional lead-based and tin-based fillers. The metallic fillers present in the joints are exposed to high temperature during the bonding, which damages the joints.

Nanoparticles of metallic materials have melting points lower than those of bulk metals [16–18]. The low melting points due to the decrease in size of materials make it possible to perform the bonding at low temperature. Bonding using metallic nanoparticles has another advantage: the nanoparticles become metallic bulk after the bonding. The metallic bulk has a melting point higher than that of the nanoparticles. As a result, the bonded materials are not released for use below their melting points.

Among electrically and thermally conductive metals, metallic Cu is promising from the viewpoints of cost and electrical migration. Our group has studied preparation of an aqueous colloid solution of metallic Cu nanoparticles by reducing the Cu^{2+} ions and CuO nanoparticles with hydrazine and metal–metal bonding processes using the metallic Cu nanoparticles [19–24]. The metallic Cu nanoparticles are oxidized easily with the oxygen in the air and the aqueous solution, which has been pointed out by several researchers [25–29]. This spoils their bonding properties, which causes their unreliability in bonding.

Cu oxide can be reduced to metallic Cu with a reducing agent or reducing atmosphere. This means that nanoparticles of Cu oxide may form metallic Cu nanoparticles during the reduction. If metal–metal bonding is performed using Cu oxide nanoparticles as the filler in a reducing atmosphere, the transformation from Cu oxide nanoparticles to metallic Cu nanoparticles and the metal–metal bonding probably take place simultaneously. The use of Cu oxide has another advantage: since Cu oxide is chemically stable in air, unlike metallic Cu, the metal–metal bonding properties of Cu oxide nanoparticles are reliable for a long period after their fabrication. From this viewpoint, nanoparticles of cupric oxide (CuO) have been examined as the filler for metal–metal bonding in our previous works [30–33]. Powder of the CuO nanoparticles was simply fabricated by mixing a copper salt aqueous solution and a sodium hydroxide aqueous solution in air at 20–80°C, and metallic Cu discs were successfully bonded using the powder.

Cuprous oxide (Cu_{2}O) is also promising as a filler since Cu_{2}O is more easily reduced thermodynamically to metallic Cu than CuO. Cu_{2}O can be produced by electrochemical reaction [34], sonication assistance [35], microwave assistance [36], and hydrothermal reaction [37]. Although these methods work well, they need processes other than chemical reactions that complicate the production processes. Cu_{2}O can also be produced with Fehling’s reagent [38]. The final solution contains sulfate, potassium sodium tartrate, and a reductant such as glucose as well as Cu ions, which may function as impurities that deteriorate the bonding properties.

In a preliminary experiment, Cu_{2}O was produced by optimizing the concentrations of raw chemicals in a reaction between Cu(NO_{3})_{2} and NaBH_{4} in aqueous solution. Because this method consisted of only mixing Cu(NO_{3})_{2} aqueous solution and NaBH_{4} aqueous solution, it was simple like the CuO production. The aim of the present work is to find a method for producing Cu_{2}O nanoparticles. The metal–metal bonding properties of the Cu_{2}O particles were also studied.

## 2. Experimental work

### 2.1. Chemicals

Copper (II) nitrate trihydrate (Cu(NO_{3})_{2}·3H_{2}O) (Kanto Chemical Co., Inc., 77.0–80.0% (as Cu(NO_{3})_{2})) and sodium borohydride (NaBH_{4}) (Kanto Chemical Co., Inc., >92%) were used as Cu_{2}O precursors. All chemicals were used as received. Water that was ion-exchanged and distilled with Yamato WG-250 was used in all the preparations.

### 2.2. Preparation

Colloid solutions of Cu_{2}O nanoparticles were synthesized by using a reaction between copper ions and reductant. An aqueous solution of NaBH_{4} was added to a Cu(NO_{3})_{2} aqueous solution under vigorous stirring at 20–80°C. Our research group has studied on development of copper-related nanoparticles for metal–metal bonding for several years, in which the nanoparticles were produced from an aqueous solution of copper salt. According to Wu and Chen’s work producing metallic Cu nanoparticles in aqueous solution [39], concentrations of copper salt were adjusted to 0.01 M in those studies, which was within their concentrations. Thus, the initial concentration of Cu(NO_{3})_{2} was also adjusted to 0.01 M in the final solution in the present work. An expected chemical equation for the reduction is 4Cu^{2+} + 4BH_{4}^{-} + 8OH^{-} → 8OH^{-} + 4H_{2}O + 4Cu[40]. The metallic Cu is formed at a stoichiometric ratio of 4:1 of Cu^{2+}:NaBH_{4} in the reduction. The NaBH_{4} concentrations were adjusted to 0.01–0.03 M in the final solution in the present work, which were higher than the stoichiometric ratio. A preliminary experiment confirmed that color of the solution turned dark after the addition of NaBH_{4}, which implied a progress of reaction. The color turning almost finished over 5 min after the NaBH_{4} addition, so that the reaction was regarded as having been almost completed in 5 min. The reaction time was adjusted to 3 h in the present work to complete the reaction.

### 2.3. Characterization

The particles were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and thermal analysis (TG-DTA). The XRD measurements were performed with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA with CuKα radiation. For preparing a powder sample for the XRD measurement, supernatant of the particle colloid was removed by decantation, and then the residue of the colloid was dried at room temperature for 24 h in vacuum. TEM photographs were taken with a JEOL JEM-2100 microscope operating at 200 kV. Samples for the TEM were prepared by dropping and evaporating the particle colloid on a collodion-coated copper...
grid. Dozens of particle diameters in the TEM images were measured to determine the number-averaged particle size and standard deviation of particle size distribution. The XPS spectra were obtained using a JEOL JPS-9010 equipped with a monochromatic Mg Kα radiation source (200 W, 10 kV, and 1253.6 eV). The XPS samples were powders that were obtained by drying the particles at room temperature in vacuum after the final removal of the supernatant during the washing process. To study the composition below the surface, the particles were etched using 500 kV Ar⁺ sputtering. To clean the particle surface, etching was performed once prior to the main measurements. Thermal analysis was performed in 3% (v/v) H₂/N₂ gas at a heating rate of 10 °C/min with a Mettler-Toledo TGA/SDTA851 thermal analyzer. Samples for thermal analysis were obtained in the same manner as that for the XRD samples.

The metal-metall bonding properties were investigated with the same set-up as used in our previous works [41-44]. Powder samples were sandwiched between copper discs (stage diameter: 10 mm, thickness: 5 mm) and plate (diameter: 5 mm, thickness: 2.5 mm), and pressed at 1.2 MPa under annealing in H₂ at 400 °C for 5 min with a Shinko Seiki vacuum reflow system. To examine the bonding strength, shear strengths that were required to separate the bonded plate and the stage were measured with a Seishin SS-100KP bond tester. To investigate the microstructure of the particle layer-to-stage joint after the measurement of shear strength, the joint was embedded with resin and then cross-sectioned, metallographically polished, and observed with a Hitachi S-4800 scanning electron microscope (SEM) operating at 30 kV. The copper plate was observed with a JEOL JSM-5600LV microscope after the measurements of shear strengths. The microstructure of the crystal orientation of the particles after the measurements of shear strengths was characterized by electron backscatter diffraction (EBSD). The EBSD was performed with a Hitachi SU-70 field emission SEM (FE-SEM) operating at 5 kV, which was equipped with an EDAX/TSL orientation imaging microscopy (OIM) system operating with an acceleration voltage of 20 kV, measured area of 3 μm x 6 μm, and measurement step of 20 nm. The sample for the EBSD was fabricated by finishing the cross-sectional sample with polishing oil and milling the finished sample with an Ar-ion milling instrument operating at an accelerating voltage of 15 kV for 180 s.

3. Results and discussion

3.1. Crystal structure

3.1.1. Effect of NaBH₄ concentration

Fig. 1 shows the XRD patterns of particles fabricated at various NaBH₄ concentrations and constant temperature of 40 °C. For NaBH₄ concentrations of 0.010 and 0.015 M, diffraction peaks were detected at 29.6, 36.4, 42.3, 52.5, 61.3, and 73.5 °. These peaks were assigned to the cubic phase of Cu₂O in accordance with the works of Labidi et al. [45] and Wang et al. [46] as well as JCPDS card #05-0667. This result indicated that Cu²⁺ was reduced to Cu⁺ to form Cu₂O. Since the amounts of NaBH₄ were small, the Cu²⁺ was not reduced to Cu⁰. The intensities of peaks due to Cu₂O decreased with increasing NaBH₄ concentration to 0.020 M. With NaBH₄ increase, new peaks appeared at 43.3 and 50.4 °. They were assigned to the face-centered cubic phase of metallic Cu in accordance with the works of Harne et al. [47] and Dong et al. [48] as well as JCPDS card #04-0836. The increase in NaBH₄ concentration promoted reduction of Cu²⁺ to Cu⁰ to form metallic Cu, though all the Cu²⁺ was not reduced to Cu⁰ because of the shortage of NaBH₄. Over 0.020 M, the intensities of Cu₂O and metallic Cu decreased further and increased, respectively, with increasing NaBH₄ concentration. The increase further promoted the reduction to metallic Cu, though the Cu₂O was still produced even at high NaBH₄ concentrations. The average crystal sizes of Cu₂O were estimated from the XRD line broadening of the 36.4° peak in accordance with the Scherrer equation. The crystal sizes were 21.2, 20.3, 13.9, 13.8, and 12.5 nm for the NaBH₄ concentrations of 0.010, 0.015, 0.020, 0.025, and 0.030 M; the size decreased with increasing NaBH₄ concentration. The increase in NaBH₄ concentration increased the rate of reduction. The increase in the reduction rate increased the number of nuclei generated in the early reaction stage, which produced a lot of fine particles. As a result, small crystallites were produced at higher NaBH₄ concentrations.

Fig. 2 shows the XRD patterns of particles fabricated at various reaction temperatures. The NaBH₄ concentrations were adjusted to 0.010 M. At this concentration only the peaks due to cubic Cu₂O were detected, as shown in Fig. 1. For all the temperatures examined, the peaks attributed to cubic Cu₂O were obtained at 36.4, 42.3, and 61.3 °. There was no large difference in peak intensities. The average crystal sizes of Cu₂O were estimated in accordance with the Scherrer equation. The crystal sizes were ca. 25 nm; the exact sizes were 29.0, 22.3, 21.2, 27.3, 21.4, 28.0, and 29.2 nm for 20, 30, 40, 50, 60, 70, and 80 °C, respectively. The crystal size was not dominantly correlated with the reaction temperature. Accordingly, the reaction
temperature was found not to be a dominant factor, which governs both the crystal structure and crystal size of Cu$_2$O particles. For 20 °C, the particle size of 111 nm was larger than the crystal size of 21.2 nm, which indicated that the Cu$_2$O particles fabricated at 0.010 M NaBH$_4$ and 40 °C were polycrystalline.

3.2. Specifications of particles

3.2.1. Nanostructure

Fig. 3 shows the TEM image of the Cu$_2$O particles fabricated with 0.010 M NaBH$_4$ at 40 °C. Several particles appeared to form an aggregate. The particle colloid solution was concentrated by drying a colloid solution dispersant in the preparation of the TEM sample, which flocculated the particles to form the aggregate. The particles were angular and had an average size of 111 ± 34 nm. The particle size was larger than the crystal size of 21.2 nm. Accordingly, the Cu$_2$O particles were polycrystalline.

Fig. 4 shows the Cu 2p$_{3/2}$ XPS spectra of Cu$_2$O particles after etching. A peak was clearly detected for each sample. The peak position increased from 932.50 to 932.59 eV with increasing the number of etchings from 1 to 5. According to the works of Ghodselahi et al. [49] and Luo et al. [50], the peak positions of (Cu$^+$—O/Cu$^0$—Cu$^0$) and Cu$^{2+}$—O are 932.3–933.8 eV.

Fig. 2 – XRD patterns of particles fabricated at temperatures of (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70, and (g) 80 °C. Initial NaBH$_4$ concentration was 0.010 M. ●: cubic Cu$_2$O.

Fig. 3 – TEM image of Cu$_2$O particles. Sample was same as in Fig. 1(a).

Fig. 4 – Cu 2p$_{3/2}$ XPS spectra of Cu$_2$O particles. Sample was same as in Fig. 1(a). CPS sample was etched by Ar$^+$ sputtering; number of etchings were (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5. Spectra were fitted with Gaussian peaks due to (●) Cu—Cu, ( ) Cu$^+$—O and ( ) Cu$^{2+}$—O bonds.
and 934.5–935.2 eV. It is difficult to distinguish the peak positions between Cu$^{+}$–O and CuO$^{-}$–CuO$^-$ because the difference in binding energy between these two bonds is only 0.1–0.2 eV in XPS analysis [49–51]. It has been confirmed in the works of Luo et al. [50] and Park et al. [52] performing Auger spectroscopy that the binding energy of CuO$^2$–CuO$^+$ is higher than that of Cu$^{+}$–O. Accordingly, the increase in peak position was considered to take place with an increase in the amount of CuO$^2$–CuO. Taking into account the possible assignments for peak positions of these bonds, the XPS spectra were fitted with a Gaussian peak using peak position, peak intensity, and FWHM (full width at half maximum) value as fitting parameters. The curve-fitting gave binding energies of 932.5, 932.7, and 933.8 eV. According to the works of Ghodselahi et al. [49], Luo et al. [50] and Mansikkamäki et al. [51], these peaks were assigned to bonds of Cu$^{+}$–O, CuO$^2$–CuO$^+$, and Cu$^{+}$–O, respectively. The XRD measurement revealed that only the peak due to CuO was detected, as shown in Fig. 1(a). Accordingly, the CuO particles were speculated to have fine cluster-like domains composed of CuO$^2$–CuO$^+$ bonds, which were too small to be detected by the XRD. Fig. 5 shows the atomic ratios of the bonds estimated from the XPS peak area intensity. The ratios of Cu$^{+}$–O, CuO$^2$–CuO$^+$, and CuO$^2$–O bonds decreased, increased, and stayed almost constant, respectively, as the etching time increased. These results indicated that the CuO particles contained the CuO$^2$–CuO bond, of which there were many at their core, and the Cu$^{+}$–O bond was distributed uniformly in them. These assignments suggested two possible routes for the production of CuO. One was some Cu$^{+}$ ions were reduced to CuO$^-$, and the rest of the Cu$^{+}$ ions were reduced to CuO to form CuO$^2$. The other was all the Cu$^{+}$ ions were reduced to CuO$^-$, and then some CuO$^-$ species were oxidized with the oxygen in the air to CuO$^+$ to form CuO.

3.2.2. Effect of annealing in reducing atmosphere

The TG-DTA curves for the CuO particles are shown in Fig. 6. In the range of 220–370 °C, an exothermic peak and a weight loss were detected, and the weights did not change above 330 °C. The CuO was reduced in the reducing gas to form metallic Cu in the temperature range. The reduction resulted in the removal of oxygen from the CuO, which caused the weight loss. In a preliminary experiment on thermal analysis of commercially available CuO, such weight loss and the exothermic peak accompanied with the weight loss took place at 570 °C. This result indicated that the CuO particles produced in the present work were reduced at a temperature lower than that of the commercially available CuO. In accordance with the XPS measurements, the CuO particles contained the CuO$^2$–CuO$^+$ bond derived from metallic Cu with low crystallinity. The metallic Cu may have functioned as a promoter for the reduction of CuO, though the detailed mechanism of the promoted reduction is still unclear.

3.3. Metal–metal bonding properties

3.3.1. Shear strength

A preliminary experiment revealed that the Cu discs were not bonded with the commercially available CuO powder, meaning that its shear strength was 0 MPa. The CuO powder was not reduced in H$_2$ gas at 400 °C in accordance with the thermal analysis. The non-reduction resulted in the lack of bonding. In contrast, the Cu discs were strongly bonded with the CuO particles fabricated in the present work, and the shear strength of the CuO particles was 27.9 MPa. It is possible that the CuO was reduced to metallic Cu, the metallic Cu grew and formed metallic Cu nanoparticles, and then the nanoparticles bonded with the Cu discs. The fine cluster-like domains composed of Cu$^0$–CuO$^-$ bonds probably promoted the growth of metallic Cu epitaxially. Consequently, strong bonding was attained with the CuO particles in the present work. The shear strength value of 27.9 MPa was comparable to the shear strength values of metallic Cu particles and CuO particles, which were recorded in our previous works [19,31]. Accordingly, this result indicated that the CuO particles could function as the filler for metal–metal bonding. Fig. 7(a) shows a photograph of the Cu stage after the measurement of shear strength. The reddish brown product that was obviously metallic Cu was widespread.
Fig. 7 – Photograph (a) and SEM image (b) of copper plate after measurement of shear strength. Powder used was Cu$_2$O particles (a) shown in Fig. 1.

on the stage. This indicated that the as-prepared particles were reduced to metallic Cu annealing at 400 °C in H$_2$ gas, which had been implied by the thermal analysis (Fig. 6). Consequently, the metallic Cu was bonded to the Cu discs. Fig. 7(b) shows an SEM image of the surface of the Cu stage after the measurement of shear strength. Sintering appeared to take place among the particles, which caused strong bonding. Dimples accompanied with sharp tips, which often form in strongly bonded regions when metallic materials are separated with shear stress [53], were not observed on the Cu disk surface. The discs appeared to be brittle fractured by the shear stress. Brittle fracture often takes place in ceramics. All the Cu$_2$O was not reduced, which left a small amount of Cu oxide in the bonded region. The existence of Cu oxide brought about by the metal–metal bonding process taking on an aspect of ceramic bonding, resulted in the brittle fracture in the present work.

3.3.2. Microstructure of particle layer
Fig. 8 shows the microstructure of the particle layer-to-Cu stage joint. Sintering of particles took place, and consequently micron-sized domains were formed. The domains and the Cu disk also sintered. This observation confirmed the strong bonding. Voids were also observed among the domains. The volume of Cu$_2$O particles decreased through their reduction to metallic Cu, which is denser than the Cu$_2$O, leading to the formation of voids.

3.3.3. Crystal orientation of particles in particle layer
Fig. 9 shows the results of the EBSD analysis for the particle layer after bonding and measurement of shear strength. Image (a) shows a band contrast map of the particle layer. Particles with light contrast were observed, and their sizes were in the range of ca. 50–300 nm that are orders of nanometer and submicron-meter. Image (b) shows a mean angular deviation map of the same place as shown in image (a). Contrast between grayish sites and blackish sites was clearly observed, which meant that the EBSD analysis was successfully performed for the particle layer. Images (c)–(e) show EBSD-determined inverse pole figure maps in the directions of the x, y, and z axes, respectively. They were obtained by analyzing the back scattering intensity in the directions in image (b). Each particle had almost a single color, which indicated that the Cu$_2$O particles became nano-sized or submicron-sized metallic Cu single crystals, or fine metallic Cu single crystals.

Fig. 8 – SEM images of plate-to-stage joint made using Cu$_2$O particles after measurement of shear strength. Images (b), (c), and (d) are high magnification images for areas surrounded with rectangles in images (a), (b), and (c), respectively. Powder used was Cu$_2$O particles (a) shown in Fig. 1.

Fig. 9 – Results of EBSD analysis for particle layer after bonding and measurement of shear strength. Image (a) shows band contrast map. Image (b) shows mean angular deviation map. Images (c), (d), and (e) show EBSD-determined inverse pole figure maps in directions of x, y, and z, respectively. Powder used was Cu$_2$O particles (a) shown in Fig. 1.
The process of annealing in H₂ gas under pressure was considered to provide not only the reduction of Cu₂O to metallic Cu, but also the formation of micron-sized domains composed of fine single crystals. The XPS measurements and the measurement of bonding strength gave rise to speculation that the epitaxial growth of metallic Cu promoted by the fine cluster-like domains composed of Cu⁶⁺–Cu⁰ bonds might have accelerated the formation of single crystals. Solid materials composed of particles with small grain size are mechanically strong compared to with large grain size due to the Hall–Petch effect [54,55]. Thus, the metallic Cu particles produced with the reduction form mechanically strong domains composed of the fine single crystals, which resulted in the strong bonding of Cu discs in the present work.

4. Conclusions

The Cu₂O nanoparticles were used as the filler for metal–metal bonding. The Cu₂O nanoparticle colloid solutions were prepared by reacting 0.01 M Cu(NO₃)₂ with 0.01−0.03 M NaBH₄ in aqueous solution at 20−80 °C. A NaBH₄ concentration of 0.01 M and reaction temperature of 40 °C resulted in the production of cubic CuO nanoparticles that had an average size of 111±34 nm and crystal size of 21.2 nm. The XPS measurements supported the hypothesis that the Cu₂O particles contained fine metallic cluster-like domains composed of Cu⁶⁺–Cu⁰ bonds. The bonding examinations in H₂ gas at 400 °C revealed that the Cu₂O particle powder had a shear strength as high as 27.9 MPa. The metallic Cu single crystalline particles, production of which during bonding was confirmed by EBSD analysis, made the metallic Cu grow epitaxially, which produced the micron-sized domains composed of fine single crystals, and consequently the metallic Cu discs were strongly bonded. Our finding that the Cu₂O nanoparticles could perform metal–metal bonding will increase interest and active research in the field of metal–metal bonding processes using nanoparticles. However, some discussions are still based on speculation. Further studies on metal–metal bonding mechanisms are awaited.

Conflicts of interest

The authors declare no conflicts of interest.

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