

Preparation of Metallic Copper Nanoparticles by Reduction of Copper Ions in Aqueous Solution and Their Metal-Metal Bonding Properties

Y. Kobayashi, T. Shirochi, Y. Yasuda, T. Morita

Abstract—This paper describes a method for preparing metallic Cu nanoparticles in aqueous solution, and a metal-metal bonding technique using the Cu particles. Preparation of the Cu particle colloid solution was performed in water at room temperature in air using a copper source ($0.01\text{ M Cu(NO}_3)_2$), a reducing reagent ($0.2 - 1.0\text{ M}$ hydrazine), and stabilizers ($0.5 \times 10^{-3}\text{ M}$ citric acid and $5.0 \times 10^{-3}\text{ M}$ cetyltrimethylammonium bromide). The metallic Cu nanoparticles with sizes of ca. 60nm were prepared at all the hydrazine concentrations examined. A stage and a plate of metallic Cu were successfully bonded under annealing at 400°C and pressurizing at 1.2 MPa for 5min in H_2 gas with help of the metallic Cu particles. A shear strength required for separating the bonded Cu substrates reached the maximum value at a hydrazine concentration of 0.8 M , and it decreased beyond the concentration. Consequently, the largest shear strength of 22.9 MPa was achieved at the 0.8 M hydrazine concentration.

Keywords—Aqueous solution, Bonding, Colloid, Copper, Nanoparticle.

I. INTRODUCTION

A technique for metal-metal bonding or connecting metallic materials is quite important mainly in fields such as metalworking industry and electronics [1],[2]. The metal-metal bonding is usually performed by annealing two or more than two metallic materials at high temperatures under pressurized [3]. In this process, components of the metallic material diffuse into the other metallic material, and consequently the metallic materials are bonded. A filler material that can diffuse easily into the materials to be bonded is inserted between them for helping the bonding. The filler materials are expected to have a low melting point, which makes it possible to bond them at low temperature and to save energy. Tin-based alloy has been widely and conventionally used as fillers or solders for metal-metal bonding, since the alloy has a melting point as low as $220\text{--}230^\circ\text{C}$. However, the bonded materials cannot be exposed at high temperature due to remelting of the tin-based alloy, which separate them.

Metallic nanoparticles are an alternative candidate as the

filler. The metallic nanoparticles are expected to have melting points lower than their bulk materials because of their large surface energy [4], [5]. The bonded materials are not separated even at high temperature, because the metallic nanoparticles are transformed to their bulk materials due to melting and fusion during bonding. From this view point, a bonding technique using metallic nanoparticles as the filler material has been proposed by several researchers [6]–[9]. The previous works have studied mainly on Ag or Ag-related nanoparticles. Though successful metal-metal bonding was attained by using the Ag or Ag-related nanoparticles, the bonding technique with their use faces at problems such as their high cost and electric migration [9], [10].

Metallic Cu takes low cost compared with Ag, and does not reveal the electric migration. Considering the problems of Ag or Ag-related nanoparticles and the advantage of metallic Cu, we have studied on metallic Cu nanoparticles and Cu-related nanoparticles as new metallic nanoparticle fillers for the past few years [11]–[18]. In our previous work, colloid solutions of metallic Cu nanoparticles were prepared by reducing Cu salts with hydrazine in aqueous solutions [15]. Their bonding abilities were dependent on hydrazine concentration in the case of copper (II) acetate ($(\text{CH}_3\text{COO})_2\text{Cu}$) used as a raw chemical. The present work studies on dependence of bonding property on hydrazine concentration by using Cu salts other than $(\text{CH}_3\text{COO})_2\text{Cu}$ toward making of a guideline for fabricating metallic Cu nanoparticles that function as the filler.

II. EXPERIMENTAL

A. Chemicals

A source of metallic Cu nanoparticles was copper nitrate trihydrate ($\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (77–80% (as $\text{Cu(NO}_3)_2$)). Citric acid monohydrate ($>99.5\%$) and cetyltrimethylammonium bromide (CTAB) (99%) were used as stabilizers. A reducing reagent used was hydrazine monohydrate ($>98.0\%$). All chemicals were purchased from Kanto Chemical Co., Inc., and were used as received. Water that was ion-exchanged and distilled with Shimadzu SWAC-500 was used in all the preparations, and was deaerated by bubbling with N_2 gas for 30 min prior to preparation of $\text{Cu(NO}_3)_2$ aqueous solutions containing citric acid and CTAB.

B. Preparation

Colloid solutions of Cu nanoparticles were prepared by reducing copper ions with reducing reagent in the presence of

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stabilizers. Hydrazine was added to $\text{Cu}(\text{NO}_3)_2$ aqueous solution containing citric acid and CTAB under vigorous stirring at room temperature in air. Initial concentrations of $\text{Cu}(\text{NO}_3)_2$, hydrazine, citric acid and CTAB were 0.01, 0.1–1.0, 0.5×10^{-3} and 5.0×10^{-3} M, respectively. The reaction time was 3h. The particles produced were washed with a process composed of centrifugation at 10000rpm, removal of supernatant, addition of water, and shake of the mixture with a vortex mixer for dispersing the particles several times.

C. Characterization

The obtained particles were characterized by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). An XRD pattern was recorded with an X-ray diffractometer (Rigaku RAD-C) operated at 20kV and 40mA with $\text{CuK}\alpha$ radiation. XRD samples were powder obtained by drying the particles at room temperature in vacuo after the final removal of supernatant. TEM was performed with a JEOL JEM-2000FX II microscope operating at 200 kV. Samples for TEM were prepared by dropping and evaporating the nanoparticle suspensions on a collodion-coated copper grid. Particle diameters in TEM images were measured to determine volume-average particle size.

Metallic bonding property was investigated by the same set-up as used in our previous works [19]–[22]. Powder samples, which were produced with the same way as the XRD samples, were sandwiched between metallic Cu discs (a metallic Cu plate (diameter: 5mm, thickness: 2.5mm) and a metallic Cu stage (diameter: 10mm, thickness: 5mm)), and pressed at 1.2 MPa under annealing in H_2 at 400°C for 5min with a Shinko Seiki vacuum reflow system. For investigation of bonding properties, shear strengths, which were required to separate the bonded plate and stage, were measured with a Seishin SS-100KP bond tester. The copper disc was observed with a JEOL JSM-5600LV microscope after the measurements of shear strengths.

III. RESULTS AND DISCUSSION

A. Morphology of Particles

Fig. 1 shows TEM images of particles prepared at various hydrazine concentrations. Many quasi-angular particles were produced for all the hydrazine concentrations examined. Sizes of the particles were 61 ± 23 nm for 0.2 M, 53 ± 14 nm for 0.4 M, 57 ± 18 nm for 0.8 M and 60 ± 19 nm for 1.0 M. There was no large difference among the samples. Fig. 2 shows XRD patterns of those particles. Peaks attributed to those of metallic Cu (face-centered cubic) (JCPDS card No. 4-0836) were detected at 43.3, 50.3 and 74.2 degree for all the particles prepared. Besides, the pattern showed several peaks for the hydrazine concentration of 0.2 M. Peaks assigned to Cu_2O (cubic) (JCPDS card No. 5-0667) were detected at 36.5, 42.4 and 61.4 degree, and to CuO (monoclinic) (JCPDS card No. 5-0661) at 35.8 (a shoulder peak) and 38.7 degree. These results indicated that most Cu ions were reduced above a certain threshold between 0.2 and 0.4 M. Average crystal sizes of the metallic Cu particles, which were estimated from the XRD line

broadening of the 36.5 degree-peak according to the Scherrer equation, were 34.4, 35.9 and 34.6 nm for the hydrazine concentrations of 0.4, 0.8 and 1.0 M, respectively. Because the metallic Cu particle sizes obtained from the TEM observation were larger than the crystal sizes, the metallic Cu particles were polycrystalline.

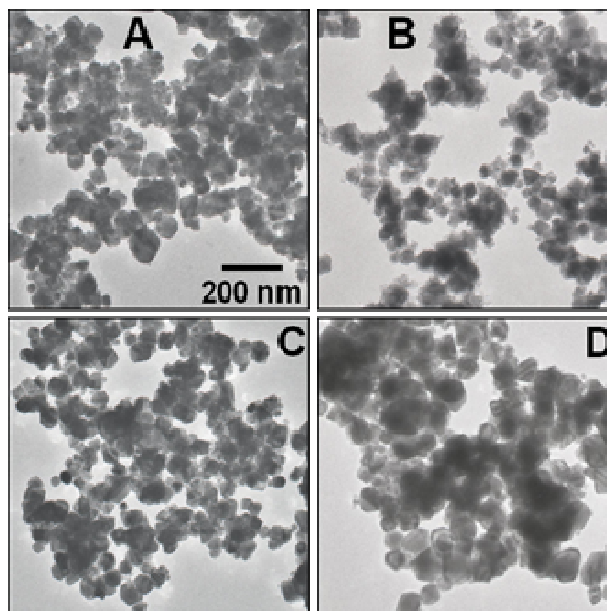


Fig. 1 TEM images of particles prepared at hydrazine concentrations of (A) 0.2, (B) 0.4 (C) 0.8, (D) 1.0 M. Concentrations of $\text{Cu}(\text{NO}_3)_2$, citric acid and CTAB were 0.01, 5.0×10^{-4} and 5.0×10^{-3} M, respectively

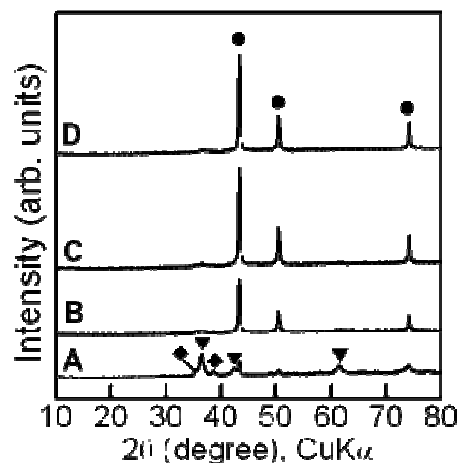


Fig. 2 XRD patterns of particles. The samples were the same as those in Fig. 1. ●: metallic Cu, ▼: Cu_2O , ◆: CuO

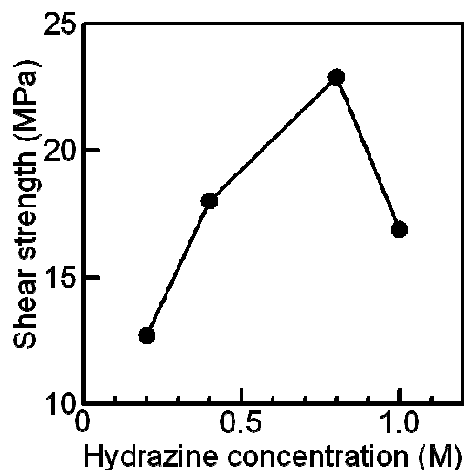


Fig. 3 Shear strength of the particles vs. hydrazine concentration in preparation, the samples were the same as those in Fig. 1

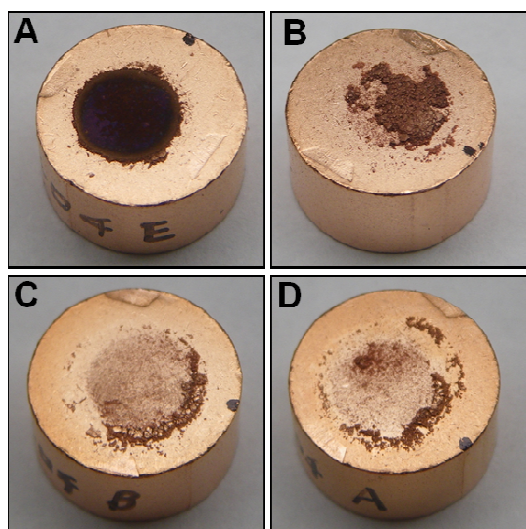


Fig. 4 Photographs of the copper plates after the measurements of shear strength. The particles used for the measurement were the same as those in Fig. 1

B. Bonding Properties

Fig.3 shows the shear strength of particles as a function of the hydrazine concentration. The shear strength increased, as the hydrazine concentration increased in the range of 0.2-0.8 M, and a shear strength as high as 22.9MPa was achieved at the hydrazine concentration of 0.8M. According to the XRD measurement (pattern A in Fig. 2), a large amount of Cu oxide was contained in the particles for the hydrazine concentration as small as 0.2 M. Removal of oxygen from the Cu oxide probably took place during the bonding at 400°C in H₂ gas, which was supported with thermal analysis performed for metallic Cu particles containing Cu oxide produced from (CH₃COO)₂Cu in our previous work [15]. The oxygen removal provided production of voids in the particles after bonding, which prevented the generated metallic copper from having efficient

contact with other particles and the copper disc. As a result, the shear strength was small at the small hydrazine concentration. Above 0.8 M, an increase in hydrazine concentration up to 1.0 M decreased the shear strength. At the high hydrazine concentrations, much hydrazine unreacting with copper ions was probably remained in the solution. Possibly, the remained hydrazine was also contained in the particles, which resulted in production of voids in the particles through removal of them in bonding at high temperature. Accordingly, the shear strength was small at the high hydrazine concentration.

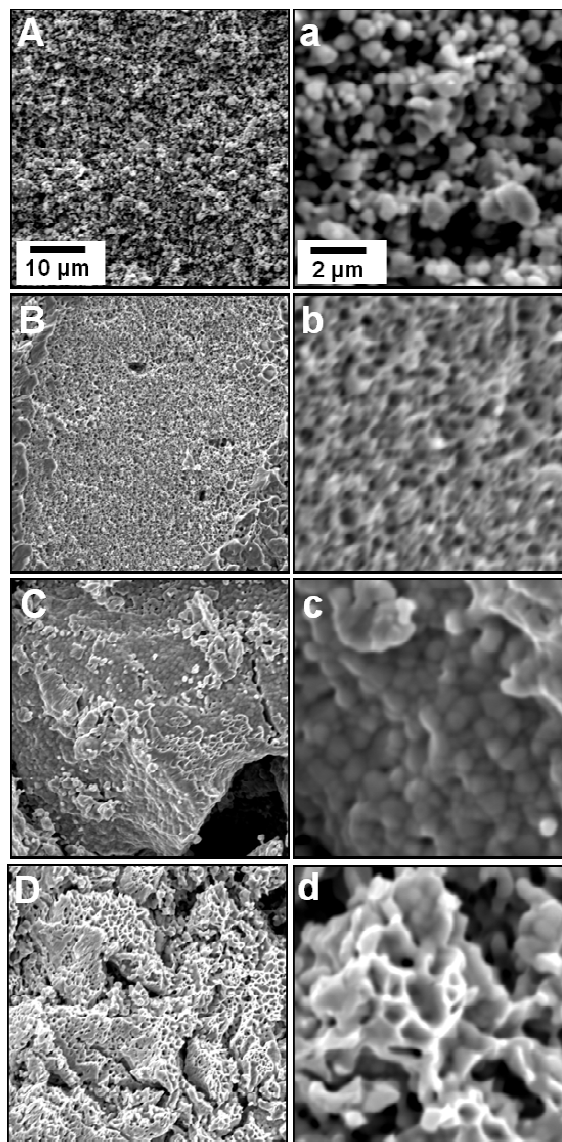


Fig. 5 SEM images of the copper plates after the measurements of shear strength. The particles used for the measurements were the same as those in Fig. 1. Images (a), (b), (c) and (d) are high magnification images of the images (A), (B), (C) and (D), respectively

Fig.4 shows photographs of the copper stages after the

measurement of shear strength. Black object was left on the stage for the hydrazine concentration of 0.2M. The black object appeared to be CuO. The XRD measurement (patternA in Fig. 2) revealed the existence of CuO in the as-prepared particles. This indicated incomplete reduction of the CuO during the bonding. Accordingly, the small shear strength was also provided by the incompleteness of reduction. At 0.4 M, some brown objects were observed in wide area on the stage. The brown objects appeared to be mixture of metallic Cu and Cu₂O. Since the Cu₂O was still remained, the shear strength was not so high compared to that for 0.8 M. Above 0.6 M, unifying of the powder and the stage as one body was achieved, though brown powders were also observed partially on the stage.

Fig. 5 shows SEM images of the copper disc surface after the measurement of shear strength. Morisada et al.'s reported that dimples accompanying with sharp tips formed when strongly-bonded sites were torn off with shear stress [9]. Similar dimples also formed on the whole surface for (CH₃COO)₂Cu, of which shear strength was as high as 37.7 MPa, as reported in our previous work [15]. In contrast, dimples were partially or locally produced on the surface, and they accompanied with no such sharp tips in all the samples examined in the present work. The shear strengths shown in Fig. 3, which were smaller than those for the (CH₃COO)₂Cu, appeared to reflect the formation of dimples with no such sharp tips. However, a mechanism for the difference in shear strength between Cu(NO₃)₂ and (CH₃COO)₂Cu is still unclear.

IV. CONCLUSIONS

A synthesis method of metallic Cu nanoparticles in aqueous solution was proposed. The colloid solutions of metallic Cu nanoparticles that had the size of ca. 60nm were prepared by reducing of 0.01M Cu ions derived from Cu(NO₃)₂ with 0.2-1.0M hydrazine in the presence of 5.0×10^{-4} M citric acid and 5.0×10^{-3} M CTAB in water at room temperature in air. The shear strength required for separating metallic Cu discs, which were bonded by inserting the Cu particle powder between the discs and annealing them at 400°C in an atmosphere of H₂ gas, was dependent on the hydrazine concentration. The incompleteness of reduction of Cu ions provided the presence of copper oxide in the particles fabricated at the low hydrazine concentration, and the unreacting hydrazine remained in the particles at the high hydrazine concentration, which provided the formation of voids in the particles through removal of them in bonding at high temperature. As a result, the low shear strengths were recorded at the low and high hydrazine concentrations. The largest shear strength of 22.9MPa was attained for the 0.8 Mhydrazine.

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