# Development of a Method for Synthesizing Ag/Cu Composite Nanoparticles and Their Bonding Property

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**Abstract:** The present work describes synthesis of Ag/Cu composite nanoparticles in aqueous solution, and metal-metal bonding in hydrogen gas or nitrogen gas using the nanoparticles. Synthesis of the Ag/Cu composite nanoparticles was performed by the following process. First, a colloid solution of metallic Cu nanoparticles was prepared by reducing copper ions using hydrazine in an aqueous solution containing citric acid and polyvinylpyrrolidone. Then, metallic Ag nanoparticles were fabricated by reducing silver ions with hydrazine in the presence of the metallic Cu nanoparticles. The metallic Ag nanoparticles with a size of ca. 25 nm were immobilized on the metallic Cu nanoparticles with sizes of 60-120 nm. Cu-Cu bonding was performed by pressurizing metallic copper discs sandwiching the nanoparticles as a filler at 1.2 MPa for 5 min under annealing in hydrogen gas or nitrogen gas. The shear strength, which was required to separate the bonded discs, recorded 26.8 and 12.1 MPa for the bonding in hydrogen gas and nitrogen gas, respectively.

Keywords: Metallic copper, metallic silver, nanoparticle, filler, meta-metal bonding.

## 1. Introduction

Currently in various industries such as automobile, civil engineering, construction industry and electronics industry, a metal-metal bonding is one of the most significant techniques. Pb-Sn solder, or filler has been used in various metal-metal bonding processes, because of its low melting point; the bonding desires low energy with no thermal damage to bonded sites.

The use of Pb has been limited, since Pb has toxicity property, which affects the environment as well as human health. Accordingly, development of Pb-free alloy fillers is quite a significant matter [1]-[4]. Recently, Sn-based alloys like Sn-Cu have been paid attention for replacements of the Pb-based fillers, since the Sn-based alloys also have low melting points. If metal components like engines of vehicles that are manufactured by the bonding process using the Sn-based alloy filler are exposed to high temperature, thermal damage to the bonded metal components, or remelt of the filler between the bonded metals takes place, which releases the bonded metals [5]. Accordingly, though the fillers with low melting points can be used for low-temperature metal-metal bonding, they are not suitable for metal-metal bonding of materials exposed to high temperature.

Nanoparticles have special properties that differ from those of bulk materials as a consequence of their small size. Representative special properties are given as catalysis [6]-[8], magneticism [9], and melting

point depression [10], [11]. The melting point depression property enables metallic nanoparticles to be used as fillers for metal-metal bonding performed at low temperature. The metal nanoparticles become bulk material after the bonding, so that the filler between the bonded metals does not remelt even for exposure to high temperature.

Metallic nanoparticles of Ag [12]-[15] and Cu [16]-[18] function as the filler. These nanoparticles have attracted extensive attention because of their high electrical conductivity. The Ag is chemically stable, promising that the Ag nanoparticle filler has a reliable bonding ability. However, concerns over its high cost and poor anti-migration property should be swept off. The Cu is also promising due to its lower cost and excellent anti-migration property. However, it tends to be oxidized in air, which provides unreliable bonding ability.

Kim et al. reported that the formation of Ag/Cu composite nanoparticles prevented metallic Cu from being oxidized [19], which expects metallic Cu nanoparticles containing metallic Ag nanoparticles to have a reliable bonding ability. Yan et al. reported performance of metal-metal bonding with the use of Ag/Cu composite nanoparticles [20]. Our research group has also studied on fabrication of Ag/Cu composite nanoparticles and investigated their metal-metal bonding property [21], [22]. The process for fabricating the Ag/Cu composite nanoparticles is complicated, since it is composed of fabrication of Cu oxide nanoparticles, reduction of the Cu oxide nanoparticles to metallic Cu nanoparticles, and reduction of Ag<sup>+</sup> in the presence of the Cu metal nanoparticles. For simplify the process, we proposed a method for producing Ag/Cu composite nanoparticles [23]. The method was composed of only one step: The Ag/Cu composite nanoparticles were fabricated by simultaneous reduction of Ag<sup>+</sup> and Cu<sup>2+</sup> using hydrazine with polyvinylpyrrolidone (PVP) and citric acid as stabilizers. Their bonding abilities for performance of Cu-Cu bonding in nitrogen gas or hydrogen gas were not very high: The formation of composite nanoparticles did not have a positive effect in the work. It is speculated that the Ag components were present not only on particle surface but also inside particles, and the presence of Ag components inside the metallic Cu nanoparticles prevented the metallic Cu nanoparticles from growing to metallic bulk, so that the simultaneous reduction method did not intensively work for bonding performance.

From this view point, the present work proposes an alternative method for fabricating the Ag/Cu composite nanoparticles. The method is composed of reduction of the  $Cu^{2+}$  to produce metallic Cu nanoparticles, and reduction of Ag<sup>+</sup> to produce metallic Ag nanoparticles in the presence of the metallic Cu nanoparticles to immobilize the metallic Ag nanoparticles on the metallic Cu nanoparticle surface. The Ag nanoparticles are expected not to be inside the composite particles, which promotes the metallic Cu particle growth, and the following metal-metal bonding. Their metal-metal bonding property was also investigated.

#### 2. Experimental

#### 2.1. Chemicals

Starting chemicals used for producing the Ag/Cu composite nanoparticles were copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) (77.0%–80.0% as Cu(NO<sub>3</sub>)<sub>2</sub>) and silver nitrate (AgNO<sub>3</sub>) (99.8% as AgNO<sub>3</sub>), respectively. Hydrazine monohydrate (>98.0%) was used as a reducing reagent for metal ions. Citric acid monohydrate (>99.5%) was used as an agent that chemically stabilizes Cu nanoparticles. PVP (K-30 (Mw=40000)) was used as a dispersing agent in preparation of nanoparticles. All chemicals were purchased from Kanto Chemical Co., Inc., and were used as received. Water that was purified by ion-exchange with a distillation apparatus (Advantech RFD372NC) was used in all preparations.

#### 2.2. Preparation

A method for preparing a colloid solution of Ag/Cu composite nanoparticles is composed of two

processes. One is production of precursor metallic Cu nanoparticles, and the other is production of metallic Ag nanoparticles in the presence of the metallic Cu nanoparticles. A colloid solution of metallic Cu nanoparticles was prepared by adding hydrazine to aqueous solution containing  $Cu(NO_3)_2$ , citric acid, and PVP with vigorous stirring at 40°C. After 1h, a AgNO<sub>3</sub> aqueous solution and hydrazine were added to the metallic Cu nanoparticle colloid solution to reduce Ag<sup>+</sup> ions in the presence of Cu nanoparticles. The reaction time was 2 h. Initial concentrations of Cu, Ag, hydrazine, citric acid, and PVP were 0.0075 M, 0.0025 M, 0.6 M, 0.00025 M, and 1.0 g/L, respectively.

## 2.3. Characterization

The nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). The TEM was performed with a JEOL JEM-2100 microscope operating at 200 kV. Samples for TEM were prepared by dropping and evaporating a particle colloid on a collodion-coated copper grid. The diameters of dozens of particles in the TEM images were measured to determine the number-averaged particle size and the standard deviation of the particle size distribution. The XRD data were collected using a Rigaku Ultima IV X-ray diffractometer equipped with a CuK $\alpha$ 1 radiation source operated at 40 kV and 30 mA. The powder samples for XRD measurement were prepared by removing the supernatant of the particle colloid solution using decantation and then drying the residue at room temperature for 24 h under vacuum. The surface composition of the particle was analyzed by the XPS using a JEOL JPS-9010 photoelectron spectrometer. The XPS spectra were recorded using Mg-K $\alpha$  radiation (200 W, 10 kV, and 1253.6 eV). The XPS samples were the same as the XRD samples. To investigate the composition below the surface of the powder samples, the particles were etched using 500 kV Ar<sup>+</sup> ion sputtering.

The metal-metal bonding properties of the nanoparticles were investigated with a process composed of metal-metal bonding and measurement of bonding strength. The nanoparticle powder, which was obtained with the same process as that for the XRD sample, was sandwiched between a metallic copper stage disc with a diameter of 10 mm and a thickness of 5 mm and a metallic copper plate disc with a diameter of 5 mm and a thickness of 2.5 mm. The discs sandwiching the powder were pressed at 1.2 MPa while being annealed under nitrogen gas or hydrogen gas at 400°C for 5 min using a Shinko Seiki vacuum reflow system. For bonding strength measurement, the shear strength required to separate the bonded discs was measured with a Seishin SS-100KP bond tester.

## 3. Results and Discussion

## 3.1. Morphology of Particles

A TEM image of the Ag/Cu nanoparticles is shown in Fig 1. Smaller particles with a size of ca. 25 nm appeared to be immobilized on larger particles with sizes of 60-120 nm.

Fig. 2 shows an XRD pattern of the particles. Peaks were recorded at 43.3, 50.4 and 74.1 degree. These peaks were assigned to (111), (200) and (220) planes of cubic copper (JCPDS card No. 04-0836), respectively. Besides the peaks due to cubic copper, peaks were detected at 38.1, 64.4, and 77.5 degree, though some peaks were faint. They were assigned to the (111), (220), and (311) planes of cubic Ag metal (JCPDS card No. 04–0783), respectively. Though a peak due to (200) plane of cubic Ag should have appeared at 44.3 degree, the peak was not clearly detected because of overlap of the peak due to (200) plane of cubic Ag and the peak of (111) plane of cubic Cu. These results indicated production of both Ag metal and Cu metal. Crystal sizes of the Cu and Ag metals were estimated on the basis of the (111) metallic Cu and Ag peaks, respectively, using the Scherrer equation. The crystal sizes of Cu metal and Ag metal was 31.7 and 10.8 nm, respectively.



Fig. 1. TEM image of Ag/Cu nanoparticles.



Fig. 3 shows the Ag + Cu atomic ratios estimated from the XPS peak area intensity. For the as-prepared Ag/Cu particles, the atomic ratios of Cu and Ag were 70 and 30 atom%, respectively. The atomic ratios increased and decreased as the etching time increased, respectively. Those ratios reached 78 and 22 atom%, respectively, at an etching number of 5. These results indicated that many species of Ag were present not inside the particles but on the particle surface. This indication implied that the large and small particles observed by the TEM (Fig. 1) were the metallic Cu and Ag nanoparticles, respectively, *or* the metallic Ag nanoparticles were immobilized on the metallic Cu nanoparticles.



Fig. 3. Atomic ratios of Ag + Cu for the surfaces of the Ag/Cu nanoparticles as a function of the number of  $Ar^+$  etching steps. (•) Cu, (•) Ag.

## 3.2. Bonding in Hydrogen Gas

Bonding of the copper discs was performed in hydrogen gas for preventing the particles from being oxidized during bonding. Fig. 4 (a) shows a photograph of the copper stage disc after measurement of shear strength. Brown products that were obviously metallic Cu were observed in widespread area on the stage. This observation indicated that the nanoparticles were not oxidized, and still metallic Cu. A shear strength was as high as 26.8 MPa (Table 1). Since there is a mismatch in *d*-spacing between Cu and Ag metal, the presence of metallic Ag nanoparticles will deteriorate bonding of metallic Cu discs. However, the discs were strongly bonded using the Ag/Cu nanoparticle powder. The Ag content in the particles of 25 mol% was so low that the Cu-Cu bonding was considered to be deteriorated. Fig. 4 (b) shows a SEM image of the disc surface after the measurement of shear strength. The nanoparticles appeared to be sintered. This observation of the particle sintering supported the strong bonding.



Fig. 4. Photograph (a) and SEM image (b) of metallic copper stage disc after measurement of shear strength. The bonding was carried out in hydrogen gas.

Table 1. Shear Strengths for Bonding in Different Atmospheres		
Atmosphere	Hydrogen gas	Nitrogen gas
Shear strength (Mpa)	26.8	12.1

## 3.3. Bonding in Nitrogen Gas

The previous section described that the copper discs were strongly bonded by performing the bonding in hydrogen gas. For safe performance of bonding in industry, the hydrogen gas was not desired to be used as atmosphere gas in the bonding. The present section describes the investigation on bonding with the use of the Au/Cu nanoparticles in nitrogen gas. Fig. 5 (a) shows a photograph of the copper stage disc after measurement of shear strength. Brown products were also observed in widespread area on the stage. The brown color was darker than that for hydrogen gas, which implied that the nanoparticles were partially oxidized during the bonding because of the dark color derived from copper oxide. According to our previous works on metallic Cu nanoparticles [24], [25], a slight amount of copper oxide is present in the particles, though the main component is metallic Cu. The copper oxide might have been slightly present on the metallic Cu surface of the Ag/Cu nanoparticles, and the copper oxide grew and revealed the dark color due to copper oxide, which implied that the copper discs were not strongly bonded compared to in hydrogen gas. Fig. 5 (b) shows a SEM image of the disc surface after the measurement of shear strength. Several particles were observed with no sintering. This observation also implied the non-strong bonding. A shear strength was 12.1 MPa (Table 1), which was lower than that of in hydrogen gas. The lower shear strength was predicted by the implications obtained by the photograph and the SEM image. Probably, the partial oxidation of the particle surface deteriorated the bonding. In our previous work on Ag/Cu nanoparticles fabricated by simultaneous reduction of  $Cu^{2+}$  and  $Ag^{+}$  in aqueous solution [23], the nanoparticle powder did not intensively help bonding of copper discs in nitrogen gas. This meant that the Ag/Cu nanoparticles produced in the present work was superior to those in the previous work for bonding in nitrogen gas. The metallic Ag and Cu components were expected to be dispersed in the particles for the simultaneous reduction, because metallic Ag and metallic Cu were simultaneously produced. In the present work, the metallic Ag was produced in the presence of the metallic Cu nanoparticles. As a result, the metallic Ag component was not dispersed inside the Ag/Cu particles but immobilized on the metallic Cu particle surface, as supported by the TEM observation and the XPS measurement. The metallic Ag component on surface was considered to cover copper oxide on particle surface and control the growth of copper oxide in an early stage of bonding. Consequently, the discs were strongly bonded even in nitrogen gas.



Fig. 5. Photograph (a) and SEM image (b) of metallic copper stage disc after measurement of shear strength. The bonding was carried out in nitrogen gas.

## 4. Conclusion

The Ag/Cu composite nanoparticles, in which the metallic Ag nanoparticles with the size of ca. 25 nm were immobilized on the metallic Cu nanoparticles with the sizes of 60-120 nm, were fabricated with the method composed of two processes. The first step was the fabrication of metallic Cu nanoparticles by the reduction of copper ions in the aqueous solution, and the second was the fabrication of metallic Ag nanoparticles by the reduction of silver ions in the aqueous solution containing the metallic Cu nanoparticles. The shear strengths required to separate metallic copper discs bonded in hydrogen gas and nitrogen gas at 400°C for 5 min while pressed at 1.2 MPa were as high as 26.8 and 12.1 MPa, respectively. The strong bonding was performed even in nitrogen, because the metallic Ag on particle surface covered copper oxide on metallic Cu surface, which helped the Cu-Cu bonding process.

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