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Original Article

Metal–metal bonding process using cuprous oxide nanoparticles

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ABSTRACT

This work performs metal–metal bonding by using cuprous oxide (Cu_2O) nanoparticles prepared by reduction in aqueous solution. A colloid solution of Cu_2O nanoparticles was prepared by mixing $Cu(NO_3)_2$ aqueous solution and $NaBH_4$ aqueous solution. Cu_2O 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 $Cu(NO_3)_2$ and 0.010 M $NaBH_4$ at a temperature of 40 °C. The Cu_2O particles contained not only Cu—O bonds but also Cu^0—Cu^0 bonds, which indicated formation of fine cluster-like domains composed of Cu^0—Cu^0 bonds. The shear strength required for separating the metallic Cu discs bonded by using the particles as a filler at 400 °C in H_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.

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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 is 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_2O) is also promising as a filler since Cu_2O is more easily reduced thermodynamically to metallic Cu than CuO. Cu_2O 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_2O 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_2O 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_2O nanoparticles. The metal–metal bonding properties of the Cu_2O particles were also studied.

2. Experimental work

2.1. Chemicals

Copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (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_2O 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_2O 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 '$4Cu^{2+} + BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O$' [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 $CuK\alpha_1$ 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

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