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Synthesis of Several Micrometer-Size Cu Particles by a Green Wet Reduction Method

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Abstract. Several micrometer-size Cu powders were synthesized by a simple and green wet-chemical process. Moreover, changes in particle size are examined with different synthesis temperatures and amounts of gelatin reducing agent. All powder samples synthesized in this study were indexed as a Cu phase despite the synthesis was performed in air. The particle size decreased with increasing the gelatin content in principle, indicating that gelatin is an effective agent in suppressing aggregation between synthesized particles. The smallest average particle size was 1.53 μm.

Introduction

Copper (Cu) powders have been studied as fillers for conductive pastes owing to their low electrical resistance and material cost [1-3]. However, pure Cu powders may oxidize in air at room temperature [4-7] and the oxidation accelerates with an increase of temperature [8,9]; thus, the fabrication and application of silver-coated Cu (Cu@Ag) powders to simultaneously possess stable electrical conductivity of Ag and the characteristics of Cu powders has recently attracted more attention [4-8,10,11]. As pitches for interconnections have become increasingly narrow [12], moreover, the fabrication of filler metal powders with diameters of several micrometers becomes more important.

Cu powders with particle sizes of several micrometers can be synthesized easily using a reduction process in solution. The fabrication of particles by the process also has merit of a minimized difference in the particle size of obtained powders [13-15]. It can also facilitate a successive Ag-plating process for the fabrication of Cu@Ag particles without any pre-treatment for the Cu particle surfaces, unlike in the fabrication of Cu@Ag using dried Cu particles. Nevertheless, report on the synthesis of Cu particles by a green wet-chemical process has been scarcely reported. This study presents a simple and green wet-chemical process to prepare Cu particles with sizes of several micrometers and a polygonal shape, and changes in size are examined with different synthesis temperatures and amounts of capping agent.

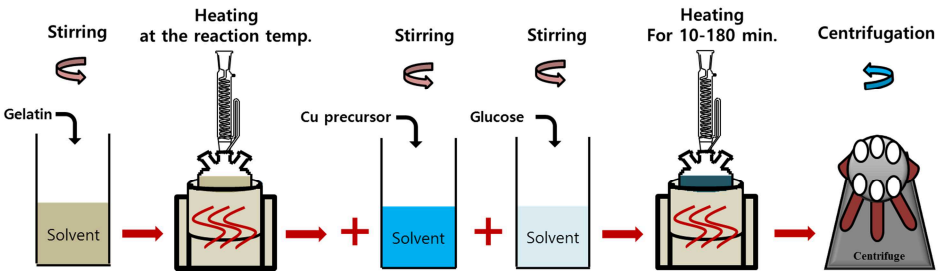

Fig. 1. Fabrication procedure for green synthesizing Cu powders with particle sizes of several micrometers.

Experimental

Cu(II) sulfate pentahydrate ($CuSO_4$, ≥98.0%, Sigma-Aldrich Co) was used as a precursor agent for synthesizing Cu particles. Gelatin (Duksan Pure Chemicals) and glucose dextrose ($C_6H_{12}O_6$,

Sigma-Aldrich Co.) were used as a green capping agent and reducing agent, respectively. Ethylene glycol (EG, $HOCH_2CH_2OH$, ≥99%, Sigma-Aldrich Co) was the solvent or medium used in this study for the reduction reaction. All the chemicals were used as received without further processing or purification.

The detailed procedure to synthesize Cu particles is as follows. Solution 1 was prepared by dissolving 2 g of gelatin with 190 mL of EG under magnetic stirring at room temperature (RT) for 30 min, and the solution was transferred to a three-neck flask. Then, solution 2 was prepared by dissolving 0.5 M of Cu(II) sulfate pentahydrate with 10 mL of EG under stirring at RT for 30 min. Lastly, solution 3 was prepared by dissolving 0.5 M of glucose with 20 mL of EG under stirring at 80 °C for 30 min. After the preparation of three solutions, the solution 2 and 3 were poured into solution 1 which is heated at specific temperature, and the mixed solution was continuously stirred at the temperature. After slight sealing the flask containing the mixed solution, the mixed solution was heated at 90–110 °C for 120 min in a mantle set and cooled for 1 h to RT. During the heating, a water chiller system was located on the flask in order to suppress the evaporation of the solvent and the pressure increase in the flask. The abovementioned procedure is presented in Fig. 1.

Powders in the solution were enriched for 5 min by centrifugation at 7000 rpm. The centrifugation was repeated 3 times with distilled water, and last one time with methanol in order to assist fast drying. The powders wetted with methanol were well dried in a low-vacuum chamber at RT. The dried powders were analyzed with a scanning electron microscope (SEM, VEGA3 LMU, TESCAN Ltd.). Determination of the average size and standard deviation of the synthesized particles was based on the SEM images. In addition, X-ray diffraction (XRD, X'pert Pro-MPD, PANalytical) was performed to confirm the composition of the dried powders.

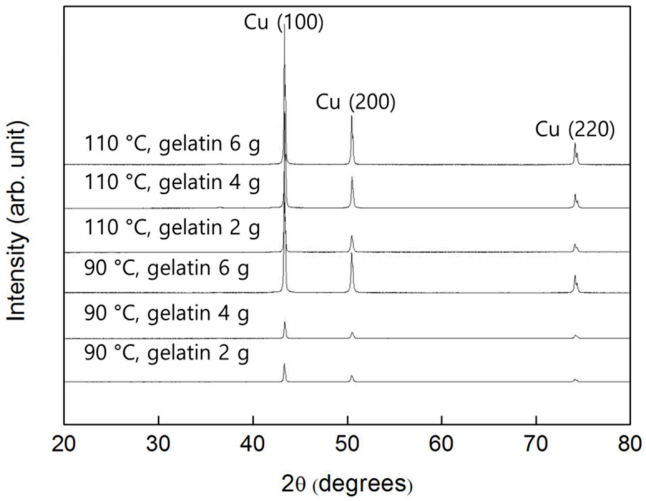

Fig. 2. XRD results of particles synthesized with different temperatures and amounts of gelatin.

Results and Discussion

Fig. 2 shows the XRD results of powders synthesized with different temperatures and amounts of gelatin. All powder samples synthesized in this study were indexed as a Cu phase and Cu oxides were scarcely detected despite the synthesis was performed in air. Compared to other research results reporting the oxidation of Cu particles during the heating for synthesis [16], these results imply that the gelatin and EG are effective constituents for system construction against oxidation of Cu.

Fig. 3 shows the SEM images and yields of Cu powders synthesized with different amounts of gelatin at 90 °C. The particle size decreased with increasing the amount of gelatin. The large particles shown in Fig. 3(a) were judged to be aggregates of the small particles shown in Fig. 3(c). Hence, it was inferred that the increase of gelatin content is more effective in suppressing aggregation between synthesized particles.

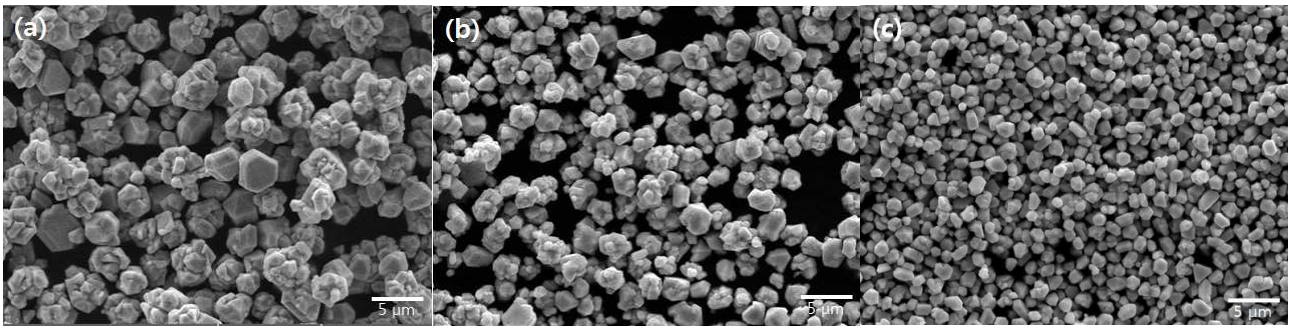

Fig. 3. SEM images of Cu particles synthesized with different amounts of gelatin at 90 °C: (a) 2, (b) 4, and (c) 6 g.

Fig. 4 shows the SEM images and yields of Cu powders synthesized with different amounts of gelatin at 110 °C. At this temperature, the simple trend which was observed in Fig. 3 was not obtained. The smallest average particle size (1.53 μm) was observed with 4 g of gelatin. However, the size definitely increased with 6 g of gelatin (Fig. 4c). The large particles in Fig. 4(c) were also observed as aggregates of small particles and many stains existed on the aggregates. These phenomena were judged to be due to the chemical transition (devitrification of blocks rich in α-amino acids) in gelatin by thermal degradation [17]. The transition may reduce effective glatin content and again hold particles together, resulting in the formation of stains on the particles. It was also inferred from the results in Fig. 4 that the transition may occur only in the case that added amount of gelatin is abundant.

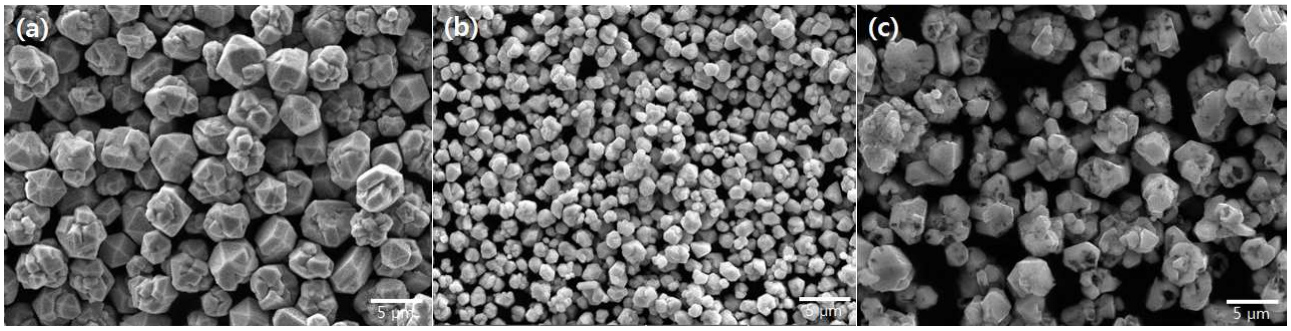

Fig. 4. SEM images of Cu particles synthesized with different amounts of gelatin at 110 °C: (a) 2, (b) 4, and (c) 6 g.

The average particle size and size deviation of Cu particles synthesized with different temperatures and amounts of gelatin are displayed in Fig. 5. Except for the sample of 110 °C and 6 g gelatin, the average size of Cu particles decreased with an increase of gelatin content at both temperatures.

Summary

Despite the synthesis was performed in air, all powder samples synthesized in this study were indexed as a Cu phase, implying that combination of gelatin and EG is effective for anti-oxidation of Cu. At 90 °C, the particle size decreased with an increase of gelatin content, indicating that gelatin plays a role in suppressing aggregation between synthesized particles. The smallest average particle size (1.53 μm) was obtained with the sample of 110 °C and 4 g. It was determined that gelatin content is crucial factor in controlling the size of Cu particles.

Acknowledgement

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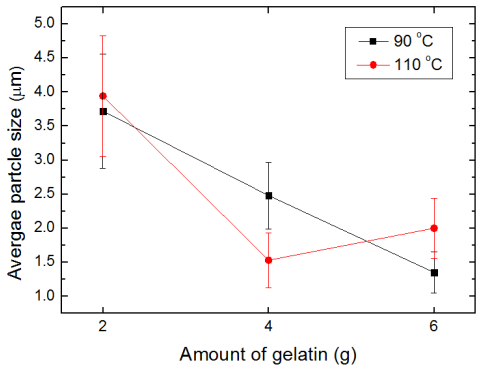

Fig. 5. Particle size distribution of Cu particles synthesized with different temperatures and amounts of gelatin.

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