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EFFECTS OF PROCESS PARAMETERS ON Cu POWDER SYNTHESIS YIELD AND PARTICLE SIZE IN A WET-CHEMICAL PROCESS

WPŁYW PARAMETRÓW PROCESU NA WYDAJNOŚĆ SYNTEZY PROSZKU Cu I WIELKOŚCI CZĄSTEK W PROCESIE MOKRYM CHEMICZNYM

This study presents a simple wet-chemical process to prepare several micron-size Cu powders. Moreover, changes in powder synthesis yield and particle size are examined with different solvents, synthesis temperatures, and amounts of reducing agent during the synthesis. As a reducing agent and capping agent, L-ascorbic acid and polyvinyl pyrrolidone were used, respectively. The yields in distilled water or an ethylene glycol (EG)/distilled water mixture were higher than that in EG alone, and the yield increased with increasing temperature owing to a lower Δ Gred value. Increasing the L-ascorbic acid concentration also increased the yield. The Cu powder synthesized in 3 h at 90°C in distilled water with 272.8 mM of L-ascorbic acid showed the lowest average particle size of 2.52 μm, indicating mechanisms of short burst nucleation and reduced growth via the increased reduction rate of Cu ions. It is estimated that the nucleation step was nearly completed within 10 min in this system. The Cu powders synthesized in an ethylene glycol/distilled water mixture presented an average particle size of 3.76 μm and the highest yield of 87.9%.

Keywords: Wet-chemical process, Micron-size Cu powder, Synthesis yield, Particle size, Gibbs free energy difference

1. Introduction

Cu powders have been extensively studied as fillers for conductive pastes in touch panel and solar cell industries because of their low resistance and material cost [1-3]. However, pure Cu powders gradually oxidize in air at room temperature [4-7] and the oxidation accelerates with increasing temperature [8,9]; thus, the fabrication and application of Ag-coated Cu (Cu@Ag) powders to suppress the surface oxidation of Cu powders has recently attracted more attention [4-8,10,11]. As pitches for interconnections have become increasingly narrow [12], the fabrication of filler metal powders with diameters of several micrometers, including Cu@Ag powders, will become more important.

Cu powders with particle sizes of several micrometers should be synthesized using a wet-chemical process because a conventional atomization method is incapable of producing such small particles although the productivity by the method is relatively low [13,14]. The fabrication of Cu by the wet-chemical process can minimize the differences in the particle size of the obtained Cu powders [15-17]. It can also facilitate a Ag-coating process for the fabrication of Cu@Ag powders without any pre-treatment for the Cu powder surfaces, unlike in the fabrication of Cu@Ag using dried Cu powders.

Use of a wet-chemical process for fabricating Cu powders with particle sizes of several micrometers has become a more crucial production technique. Nevertheless, the yield of Cu powders after synthesis by a wet-chemical process has been scarcely reported. The morphologies of the synthesized powders are also important in order to use them as fillers. This study presents a simple wet-chemical process to prepare Cu powders with particle sizes of several micrometers, and changes in yield and powder morphology are examined with different solvents, synthesis temperatures, and amounts of reducing agent.

2. Experimental

Cu(II) nitrate trihydrate (Cu[NO$_3$]$_2$·3H$_2$O, ~99%, Acros Organics) was used as a common precursor agent for synthesizing Cu powders, and polyvinyl pyrrolidone (PVP, molecular weight: 10,000) and L-ascorbic acid (C$_6$H$_8$O$_6$, reagent grade) were used as a capping agent and reducing agent, respectively. Ethylene glycol (EG, HOCH$_2$CH$_2$OH, 99%) and distilled water were the two solvents or media used in this study for the reduction reaction, and a 1:1 mixture of distilled water and EG was used as a third solvent. All the chemicals except Cu(II) nitrate trihydrate were purchased from Sigma-Aldrich Co. and used as received without further processing or purification.

The detailed procedure to synthesize Cu powders with particle sizes of several micrometers is as follows. Solution

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1 (110 mL) was prepared by dissolving 27.28 mM of Cu(II) nitrate trihydrate and 4.545 mM of PVP with a specific solvent under magnetic stirring for 2 h. Then, solution 2 (110 mL), which is prepared by dissolving 136.3 mM (the concentration criterion in the experiments) of L-ascorbic acid with a specific solvent (identical to that used in the solution 1) under magnetic stirring for 2 h was poured into solution 1, and the mixed solution was stirred for 3 min at room temperature using a magnetic bar. After slightly sealing a vial containing the mixed solution, the mixed solution was heated for 10-180 min up to 70-150°C n a mantle set and cooled for 1 h to room temperature. During the heating, a water chiller system was located on the vial in order to suppress the evaporation of the solvent and the pressure increase in the vial. The abovementioned procedure is represented in Fig. 1.
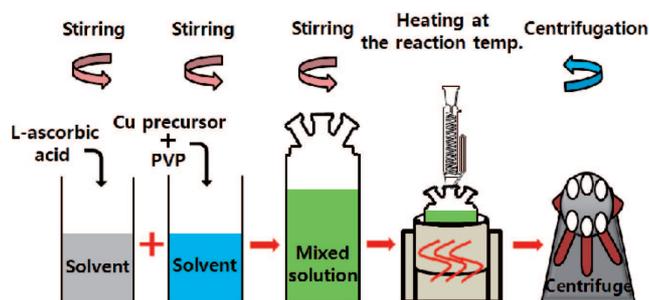

Fig. 1. Fabrication procedure for synthesizing Cu powders with particle sizes of several micrometers

Powders in the solution were enriched for 15 min by centrifugation at 7000 rpm. The centrifugation was repeated three times in order to exchange the specific solvent with methanol. The powders wetted with methanol were well dried in a low-vacuum chamber at room temperature, which was beneficial for the subsequent analysis. The dried powders were analyzed with a scanning electron microscope (SEM, S-2300, Hitachi Ltd.). Determination of the average size and standard deviation of the synthesized powder particles was based on the SEM images. Moreover, the composition of the dried powders was confirmed by X-ray diffraction (XRD, X'pert PRO-MPD, PANalytical). The synthesis yield of the Cu powders was determined by dividing the weight of the obtained dry Cu powders by the Cu weight in the initial Cu precursor.

3. Results and discussion

Fig. 2 shows the SEM images and yields of powders synthesized in 3 h with different solvent types and temperatures. All powder samples synthesized in this study were indexed as a Cu phase by the XRD results, shown in Fig. 3. The synthesis yield increased with increasing synthesis temperature for the three solvents. However, the yield changed significantly with respect to the solvent type. In other words, the synthesis yields in the distilled water or the mixture of EG and distilled water were higher than that in EG. It is estimated that the enhancement of yield is attributed to the variation of the Gibbs free energy difference (ΔG_{red}) related to the reduction of Cu ions. The solvent type and temperature might directly affect the ΔG_{red} value in the wet-chemical synthesis [18]. In these systems, it is judged that the distilled water solvent and higher synthesis temperature lowered the ΔG_{red} value to a more negative value. The particle diameters in all the synthesized samples were in the range from 3.9 to 5.9 μm, and the powders synthesized in EG (4.9-5.3 μm) were larger than those in distilled water (3.6-3.9 μm). The lower ΔG_{red} in distilled water might indicate a short burst of nucleation of Cu and reduced growth in comparison with EG, resulting in finer particle sizes.
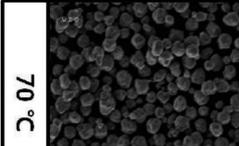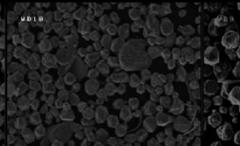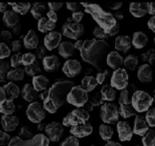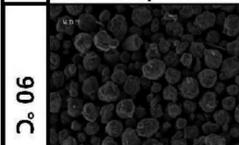

Fig. 2. SEM images and yields of Cu powders synthesized in 3 h with different solvent types and temperatures
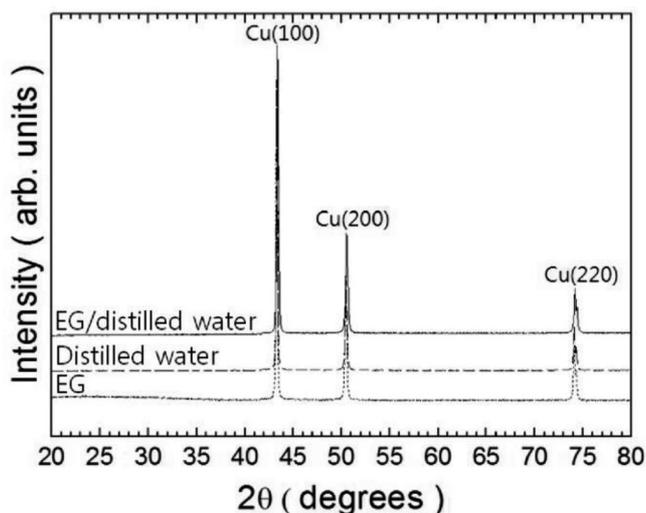

Fig. 3. XRD results of Cu powders synthesized in 3 h at 70°C with different solvent types

In order to enhance the synthesis yield of Cu powders in EG solvent, the synthesis temperature was increased up to 150°C. Fig. 4 shows the SEM images and yields of Cu powders synthesized in EG for 3 h at different temperatures. The yield increased gradually with increasing temperature. The yield obtained at 150°C in particular approached those obtained in distilled water or the EG/distilled water solvent. The particle size deviation of the synthesized powders also increased gradually with increasing the temperature.

To find out the effect of the concentration of the reducing agent on the synthesis yield, L-ascorbic acid was added in varying concentrations. Fig. 5 shows the SEM images and yields of Cu powders synthesized in 3 h at 90°C with dif-

ferent solvent types and amounts of L-ascorbic acid. Overall, the yield obtained in EG was lower than those obtained in distilled water or the EG/distilled water solvent. Furthermore, Cu powders were not formed during synthesis in EG for 3 h at 90°C. These results imply the low reductibility and reduction rate of Cu ions in the EG solvent. The increased concentration of L-ascorbic acid clearly enhanced the yield for all solvent types. However, it was also clear that the synthesis yield became saturated at high concentrations of L-ascorbic acid. It is thus verified that reductibility increased at higher reducing agent concentration.
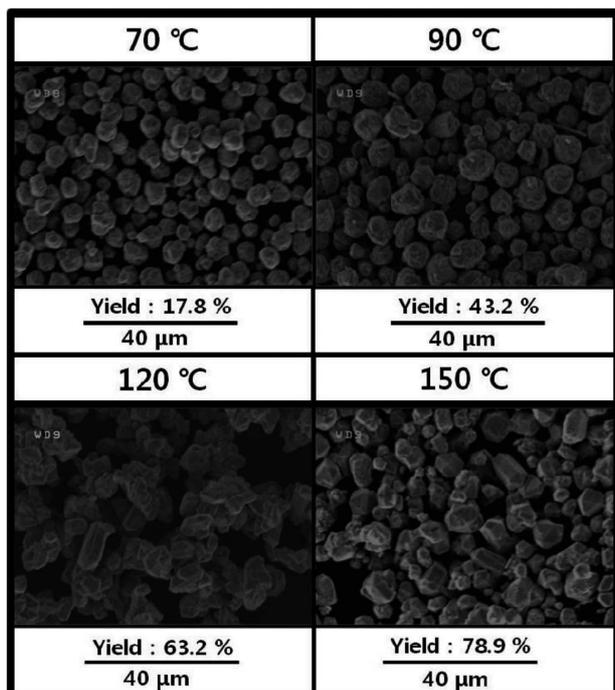

Fig. 4. SEM images and yields of Cu powders synthesized in an ethylene glycol for 3 h at different temperatures
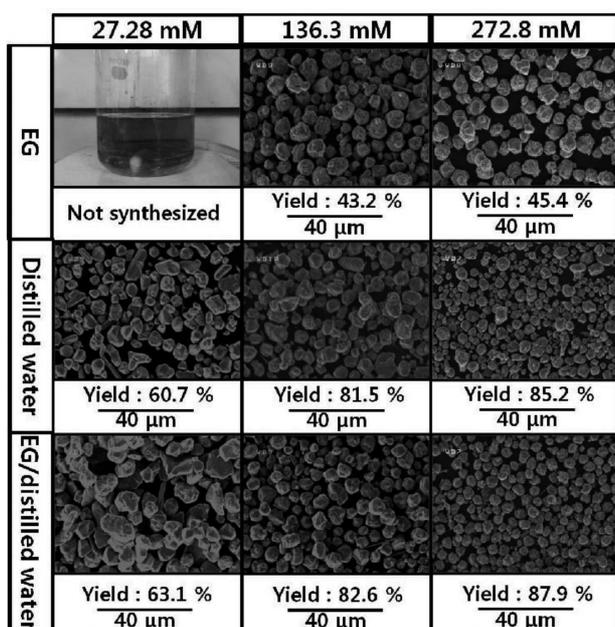

Fig. 5. SEM images and yields of Cu powders synthesized in 3 h at 90°C with different solvent types and amounts of L-ascorbic acid

The average particle size and size deviation of Cu powders synthesized in 3 h at 90°C with different solvent types when the added amount of L-ascorbic acid was 272.8 mM is displayed in Fig. 6. The average particle size of the Cu powders was the lowest in the case when distilled water solvent was used (2.52 μm), and the size deviation was the lowest with the EG/distilled water solvent. The final particle size of the synthesized powders can be explained by nucleation and growth mechanisms based on LaMer's model [15,19,20]. In the condition of a lower ΔG_{red} value (distilled water solvent), the enhanced reduction rate of Cu ions favors the generation of more nuclei during a short nucleation period, resulting in the final formation of smaller Cu particles. In other words, the final particle size decreased because the number of Cu atoms available for particle growth per growing particle decreased with the increasing number of nuclei. However, higher ΔG_{red} values (EG solvent) might permit a short nucleation period and a long growth period, resulting in the formation of larger Cu particles. The trend in which smaller particles are finally synthesized with lower ΔG_{red} would come into greater prominence at higher reducing agent concentrations, which accelerates the reduction rate, as shown in Fig. 6.
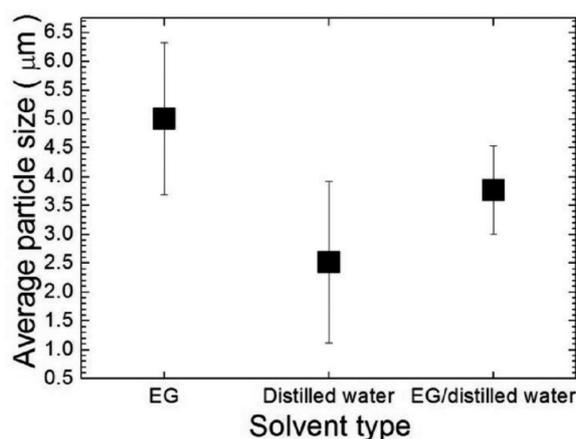

Fig. 6. Size distribution of Cu powders synthesized in 3 h at 90°C with different solvent types (the added amount of L-ascorbic acid was 272.8 mM)

Finally, the change in powder synthesis yield and particle size was observed with respect to synthesis time, keeping the solvent type and reducing agent concentration constant. The solvent type and reducing agent concentration used were those that represented both the highest yield and the minimum size deviation. Fig. 7 shows the SEM images and yields of Cu powders synthesized in a mixed solvent of EG/distilled water at 90°C with different times. With the increase of synthesis time, the yield gradually increased until reaching saturation. The size was similar in the observed time span. However, the size deviation was large initially, but it decreased with increasing time, implying that the nucleation step was nearly completed within 10 min.
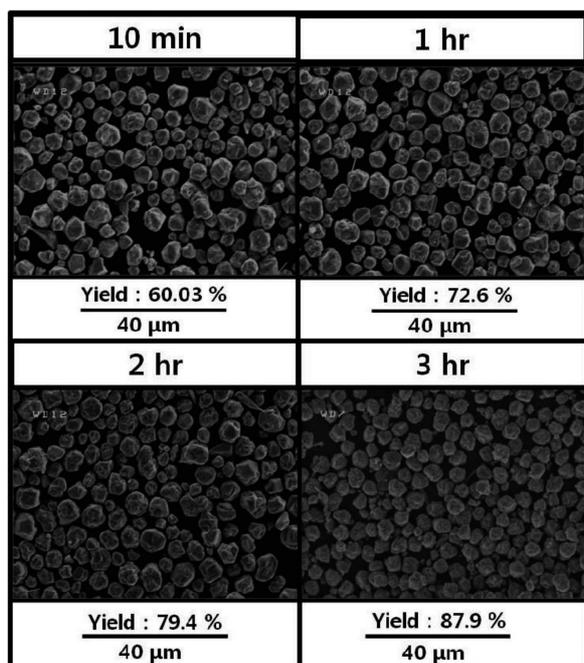
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Fig. 7. SEM images and yields of Cu powders synthesized in a mixture solvent of ethylene glycol and distilled water at 90°C with different times (the added amount of L-ascorbic acid was 272.8 mM)

4. Conclusions

Cu powders with particle sizes of several micrometers were synthesized by a wet-chemical process using L-ascorbic acid as a reducing agent. The synthesis yield and particle size were scrutinized with respect to solvent type, synthesis temperature, and added amount of L-ascorbic acid. The yields in distilled water or the EG/distilled water mixture were higher than that in EG alone, and the yield increased with increasing temperature because of lower ΔG_{red} values. Increasing the L-ascorbic acid concentration also increased the yield. The Cu powders synthesized in 3 h at 90°C in distilled water when the added amount of L-ascorbic acid was 272.8 mM showed the lowest average particle size of 2.52 μm, indicating the mechanisms of short-burst nucleation and reduced growth through the enhanced reduction rate of Cu ions. It is estimated that nucleation was nearly completed within 10 min in this system. The Cu powders synthesized in the EG/distilled water mixture presented an average particle size of 3.76 μm with the highest yield of 87.9%.

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