Growth Process of Copper Particles in the Cuprous Oxide-Water System

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Dispersed copper powder was prepared from cuprous oxide slurry by a wet chemical reduction technique with hydrazine. Palladium chloride (PdCl_2) was used to produce palladium (Pd) seed with its stabilizer, polyvinyl pyrrolidone (PVP) and sodium pyrophosphate ($\text{Na}_4\text{O}_7\text{P}_2$) was added as a dispersion agent. The formation and growth process of copper particles in the heterogeneous system were investigated in terms of reaction temperature and slurry concentration. As a general trend observed elsewhere, the average particle size of copper powder decreased from 420 nm to 150 nm with an increase of temperature from 313 to 353 K, while the shape of its number particle size distribution changed from bi-modal at low temperatures (313–323 K) to mono-modal at higher ones (333–353 K). Moreover, number size distributions of the powders produced at higher concentrations (2.5–40 g/L) all exhibit mono-modal shape while at 1.25 g/L it is bi-modal one. The explanation were based on the relationship between the number of Pd seed on the copper particles activated, which govern size and size distribution of final production in heterogeneous system, and the generation rate of Cu monomer at given conditions. [doi:10.2320/matertrans.48.1137]

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1. Introduction

Conductive pastes have been used for the formation of thick film conductors such as electrodes or conductive patterns in multilayered electronic parts and printed circuit boards. They include metal powder dispersed in an organic vehicle along with glass frit. The replacement of precious metal powders like gold, silver or palladium by copper powder for the production of conductive paste for hybrid integrated circuit and for the metallization of multilayer ceramic capacitor (MLCC) is a current trend in the electronic industry. Copper offers several economic and performance advantages over precious metals. The conductivity of copper is as good as silver and 40% better than that of gold. The stability of copper at high frequencies is better than that of gold or silver and it is compatible with most solder materials.¹⁾

A number of methods have been developed for the preparation of Cu powder. Among them, the chemical reduction of copper salts with hydrazine or hydrogen in an aqueous system has been well known.^{2,3)} However, this method suffers from agglomeration and chaotic growth of copper particles. Recently, copper oxide slurries in liquid polyols have been studied to improve the uniformity and dispersion of copper particles, but this technique requires high intensity energy and long reaction time.⁴⁾ Copper oxides slurry usually exhibits very low solubility in water, so that the replacement of solute salts by the solid oxides in wet reduction method is expected to minimize the agglomeration resulted from the strong reduction power of hydrazine or hydrogen. However, any reports to deal with the preparation of Cu powders from corresponding oxide compounds by a wet chemical reduction are hardly found.

In the present study, fine copper metal powders were prepared from a heterogeneous system of Cu_2O -water slurry by chemical reduction with hydrazine. The investigation

focused on the process parameters which play an important role on the stability of powder in liquid as well as its size and size distribution, such as reaction temperature and concentration of precursor.

2. Experimental Procedure

All chemicals used throughout the experiments are in analytical grade. Cuprous oxide (Cu_2O), polyvinyl pyrrolidone (PVP k-30) and sodium pyrophosphate decahydrate ($\text{Na}_4\text{O}_7\text{P}_2 \cdot 10\text{H}_2\text{O}$) are purchased from Junsei Chemical Co., Japan. Palladium chloride (PdCl_2) was from Kojima Chemical Reagents Inc., Japan and hydrazine monohydrate (80% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) from DC Chemical Co., Korea.

In a typical procedure, 3 g PVP was added to a 300 mL 1.15×10^{-5} M Pd^{2+} solution and mixed under a magnetic bar stirring condition. Stable palladium seeds (~ 5 nm) as shown in Fig. 1 were formed by adding 1 mL hydrazine into the solution at 313 K. This step can be understood as an attempt for achieving a short burst nucleation.

Applying the result reported by J.G. Ahn⁵⁾ a dosage of 99 mg/L $\text{Na}_4\text{O}_7\text{P}_2$, which strongly promotes zeta potential of as-formed Cu particles, was added into the above suspension along with an addition of Cu_2O in the 1.25 to 40 g/L range, and mixed in several ten seconds. Then, a hydrazine solution was slowly introduced drop by drop at 0.6 mL/min. The reaction temperature was varied from 313 to 353 K. The suspension was kept under agitation in atmospheric ambient air until the reaction completes. At the termination of each reaction, the precipitated solid particles were separated and subsequently washed with distilled water and ethanol several times. Finally, the powder was dried at 313 K in nitrogen and kept in a desiccator to minimize oxidation.

The consumption time, which is the time required to completely convert Cu_2O to Cu metal, was determined by X-ray diffraction (XRD, RTP 300PC, Rigaku, Japan) in reflection mode ($\text{Cu-K}\alpha$ radiation) for the products sampled at different time intervals. The particle size distribution of Cu

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Fig. 1 TEM image of Pd seed produced in the typical procedure.

Fig. 2 XRD pattern of the Cu powder prepared with 10 g/L Cu_2O at 333 K.

powders was measured by counting 100 particles in each picture taken by scanning electron microscopy (SEM, JEOL, JPS-9010, Japan).

3. Results and Discussion

Figure 2 shows XRD pattern of the Cu powders produced in accordance with the typical procedure described in the experimental procedure: 10 g/L Cu_2O , 99 mg/L $\text{Na}_4\text{O}_7\text{P}_2$, and 0.6 mL/min. N_2H_4 at 333 K. The well-defined copper crystalline peaks only are detected, but no oxide compound peaks are found, confirming the complete conversion from Cu_2O to Cu.

Figure 3 shows the SEM images of Cu powders produced at different reaction temperatures. Apparently, the powders show spherical in shape, well dispersed as a consequence of a 99 mg/L $\text{Na}_4\text{O}_7\text{P}_2$ addition giving rise of electrostatic repulsion.⁵⁾

Figure 4 depicts the mean size variation with reaction temperature. While the temperature varies from 313 K to 353 K, the mean particle size decreases monotonically from 420 nm at 313 K down to 150 nm at 353 K, meanwhile their number size distributions changes from bi-modal at 313 K and 323 K to mono-modal at higher temperatures as shown in Fig. 5.

In general, the size and size distribution of the final powder formed by heterogeneous nucleation depends closely on two variables: aggregation of formed particles and number of Pd seed particles. As reported by J.G. Ahn,⁵⁾ the aggregation of particles is prevented well by an addition of 99 mg/L $\text{Na}_4\text{O}_7\text{P}_2$. Thus, the number of Pd seed particles added externally will elucidate the characteristics of the resulting products formed at different temperatures.

As mentioned above, the Pd particles used as seeds in these conditions were stabilized by PVP. It is anticipated that their surface activity might be lowered by the PVP absorption layers, thus inhibiting the deposition of Cu monomers on them, leading to a significant difference between the numbers of Pd particles added and the true number activated. In other words, the inactivated Pd particles can be collected conveniently after terminating the conversions. According to this way, the number of activated Pd particles can be inferred precisely. The process for collecting inactivated Pd seed particles is represented in the reference.⁶⁾

The total number of Pd particles formed from 1.5×10^{-5} M Pd^{2+} addition and the number of Pd particles in the decanted solution are denoted as N_T and N_R , respectively. The term $\frac{N_T - N_R}{N_T} \cdot 100\%$ is defined as the weight percentage of Pd particles consumed in the Cu_2O -Cu conversion or the weight percentage of active Pd particles.

Figure 6(a) shows the weight percentage of active Pd particles increasing with an increase of reaction temperature in the investigated range (313–353 K). For instance, 22%, 51%, 55%, 66% and 73% Pd particles were consumed at 313, 323, 333, 343 and 353 K, respectively.

A rapidly decrease of consumption time resulted from an increase of reaction temperature shown in the Fig. 4 indicates a strong promotion of temperature on reaction rate. Accordingly, it is believed that at higher reaction temperature (333–353 K), larger number of Cu monomers is generated in a short duration; hence easily deposit on the PVP-absorbed Pd particles to form primary particles, which is closely related to the high trend of decreasing surface energy.⁷⁾ Whereas they would select only the most activated Pd particles for their deposition as reaction rate is low at 313 K and 323 K. In other words, at higher reaction rate conditions larger numbers of Pd particles were consumed. Considering on a constantly used Cu_2O amount of 10 g/L, a decrease of particles size of the powders followed by an increase of temperature as shown in Fig. 3 are evident.

Figure 6(b) shows the weight percentage of active Pd particles as a function of reaction time at different temperatures (313–353 K). At 313 K, it increases gradually from 0% to 22% until finishing the Cu_2O -Cu conversion after 50 minutes. Meanwhile, at 323 K, it increases from 0% to 51% following different slopes. Firstly, it increases rapidly to 40% after 5 minutes, then gradually to 48% and 50% after 10 and 20 minutes respectively, and thereafter remains nearly

Fig. 3 SEM images of Cu powders prepared with 10 g/L Cu_2O at different temperatures.

Fig. 4 Average particle sizes and consumption times as a function of temperature at 10 g/L Cu_2O .

Fig. 5 Number particle size distributions at different temperatures with 10 g/L Cu_2O .

constant throughout the rest of reaction time (30 minutes). The feature of this variation demonstrates Pd particles are first preferentially deposited with Cu monomers to form stable particles, but are not sufficient to consume completely

a further generation of Cu monomers at the given condition, resulting in an accumulation of Cu monomers in solution, thus leading to the tendency of continuously consuming the

Fig. 6 Weight percentages of active palladium particles as a function of (a) reaction temperature and (b) time at different temperatures.

rest number of Pd particles until the balance between generation of supersaturation by the reaction and consumption rate by the particle growth was well established.⁸⁾ In this respect, it can be said that a slow consumption rate of Pd particles in the conversions at 313 K and 323 K seems to be like a continuous nucleation occurred in homogeneous system, evidently yielding the powder with bi-modal number particle size distribution as shown in Fig. 4.⁹⁾

In contrarily, at 333, 343 and 353 K, 55%, 66% and 72% Pd particles respectively, were quickly consumed at early stages of the conversions (after 5 minutes), and thereafter no longer Pd particles were consumed. In other words, those numbers of Pd particles were good enough to consume completely the further generation of supersaturation at the given condition.^{8,10–13)} All particles start growing at the same point of time, thus yielding mono-modal number particle size distribution powders as described in Fig. 5.

Figure 7 shows the SEM images of the Cu powders produced at different Cu_2O concentrations (1.25–40 g/L) at 333 K following the typical procedure. The powders are roughly spherical in shape and well dispersed. This proves that the electrostatical repulsion by 99 mg/L $\text{Na}_4\text{O}_7\text{P}_2$ addition plays strong impact in highly concentrated slurry system.

Interestingly, the average particle size first decreases from 183 nm at 1.25 g/L Cu_2O down to 178 nm at 2.5 g/L Cu_2O , and thereafter monotonically increases to 354 nm at 40 g/L as depicted in Fig. 8. It has been known that the particle size of the copper usually increases as precursor concentration increases.^{4,14)} However, in the present research, this relationship seems to be no longer appropriate.

In Fig. 8, it is noticed that although Cu_2O concentrations are largely different but the consumption times show a slightly deviation. It suggests that the generation rate of Cu monomers at high Cu_2O concentrations is extremely high over than that at lower Cu_2O concentrations. In this respect, impact of Cu_2O concentration is same as that of temperature in promoting reaction rate, thus activity of Pd particles. Indeed, Fig. 9 indicates that at 1.25 g/L Cu_2O condition 14% Pd particle were consumed, while at 2.5, 5, 10, 20, 30 and

40 g/L Cu_2O conditions number of active Pd particles are equal to 28, 47, 66, 72, 81 and 86% respectively of the total Pd particles added externally.

As a general rule, an increase in number of active Pd particles usually results in a decrease of Cu particle size while an increase of Cu_2O concentration usually results in an increase of particle size. In this respect, a decrease of particle size in the range 1.25–2.5 g/L is due to the domination of the former over than the latter while an increase of particle size in the range 2.5–40 g/L Cu_2O concentration is due to the domination of the latter over than the former.

As mentioned previously, generation rate of Cu monomers at 1.25 g/L Cu_2O is too low as compared to the others. It is believed that that number of Pd particles is slowly consumed throughout the process. Therefore, the bi-modal number size distribution of the powder at 1.25 g/L as shown in Fig. 10 is because Pd particles grown at different points of time by Cu monomer deposition.

In contrarily, Fig. 10 shows that all the other powders produced in the range 2.5–40 g/L exhibit mono-modal number particle size distributions. It can be thought that the numbers of Pd particles equal to 28, 47, 66, 72, 81 and 86% might be consumed at the beginnings, are good enough to establish the balance between the generation rate of Cu monomers by the reaction and consumption rate by the Pd particles growth at 5, 10, 20, 30, 40 g/L Cu_2O conditions, thus yielding mono-modal number size distribution powders.^{8,10–13)}

In Fig. 10, it is noted that the copper powder prepared at 40 g/L Cu_2O exhibits a much wide mono-modal number distribution and its average size becomes larger, compared to the ones at 20 g/L and 30 g/L. At this high Cu_2O concentration, the generation rate of Cu monomers is very high. Fast deposition of Cu monomer on Pd particles as well as high collision frequency between them in highly concentrated system, of course, might result in uneven growth of particles, rendering the product size and its distribution larger and wider, respectively.

Fig. 7 SEM images of Cu powders produced at different Cu_2O concentrations at 333 K.

4. Conclusions

Dispersed fine Cu powders were prepared from the Cu_2O - H_2O system by a wet chemical reduction technique with hydrazine through a heterogeneous nucleation route. Palladium chloride (PdCl_2) was used to produce Pd seed particles with its stabilizer, polyvinyl pyrrolidone and $\text{Na}_4\text{O}_7\text{P}_2$ as a dispersion agent. The conversion rate continuously increased from 313 to 353 K, giving a rise in number of the active Pd particles, thus reducing mean size of the products from 420 to 150 nm, respectively. The powders produced at 313 K and 323 K is bi-modal number size distributions because of continuous consumption of Pd particles throughout conver-

sion. Whereas at 333 K, 343 K and 353 K all powders exhibit mono-modal number size distribution, because large number of Pd particles was consumed at the early stages, all particles started to grow at the same point of time.

An increase of Cu_2O concentration plays strong impact in promoting the Cu_2O -Cu conversion rate like that of temperature, thus number of active Pd particles. A decrease of particle size in the range 1.25–2.5 g/L Cu_2O is because the increase of number of active particles is dominant than the increase of Cu_2O concentration in governing the particle size. In contrarily, in the range 2.5–40 g/L the latter is dominant than the former, thus giving a rise of particle size. The explanation for mono-modal size distributions of the powders

Fig. 8 Average particle sizes and consumption times as a function of Cu₂O at 333 K.

Fig. 9 Weight percentages of active palladium particles as a function of Cu₂O concentration.

produced in the range 2.5–40 g/L is like that for the powders produced at different temperatures in the range 333–353 K, while the explanation for bi-modal size distribution of the powders obtained at 333 K and 343 K is appropriate to that produced at 1.25 g/L Cu₂O.

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Fig. 10 Number particle size distributions at different Cu₂O concentrations at 333 K.

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