Effect of gas environment on properties of particles prepared by spray pyrolysis of metal nitrates

Eun Kyung Park, Sangchun Rah, and Sun-Geon Kim†

Department of Chemical Engineering, Chung Ang University, 221, Huksuk-dong, Dongjak-gu, Seoul 156-756, Korea
(*Received 3 July 2007 • accepted 7 January 2008*)

Abstract−Particles in different states of oxidation were prepared by spray pyrolyses of aqueous solutions of silver and copper nitrates under different gas environments: air, nitrogen or mixture gas of 10 vol%H_2-N_2, respectively. Silver nitrate was converted to phase-pure silver at temperatures below 500 °C whose densification and crystallization were completed around 500 °C, irrespective of the gas environment. On the other hand, phase-pure copper(II) oxide was formed from copper nitrate up to 1,000 °C with air, but below 800 °C with nitrogen, above which copper(I) oxide was produced. Phase-pure copper particles were obtained with the mixture gas at temperatures above 400 °C. Copper(I) oxide was sintered and crystallized more easily than copper(II) oxide. The rates of the metallization, sintering and crystallization of copper were between those of silver and nickel.

Key words: Metal Particles, Spray Pyrolysis, Gas Environment, Metallization, Crystallization

INTRODUCTION

Metal particles such as palladium, silver, copper and nickel have been widely used to form conducting pastes for integrated circuits and other electronic devices [1]. The quality of the pastes mostly depends on the properties of the metal particles such as monodispersity, sphericity, solidness, dispersion without agglomeration, purity and crystallinity [2].

Recently, spray pyrolysis [3] has been one of the most promising methods to prepare nickel [4-9] and silver particles [10,11] with such properties. In order to prepare nickel particles from aqueous solution of $NiCl_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$, hydrogen was used with carrier nitrogen up to 20 vol% in the gas mixture. Such amount of hydrogen was highly excessive compared to stoichiometry but was required based on kinetic point of view to accomplish complete reduction of the precursor salt and save time sufficient for subsequent sintering and crystallization [8,9]. Without the reducing gas, nickel oxide particles were obtained by spray pyrolysis of the nickel salts [6,7,12,13]. Pluym et al. [10] prepared phase-pure silver particles above 600 °C and 900 °C with nitrogen and air, respectively. On the other hand, copper particles, whose ionization sequence was between silver and nickel, showed quite complex results. Majumdar et al. [14] prepared CuO particles with air, CuO and Cu_2O particles with nitrogen, and CuO and metallic copper particles with 93 vol% N_2-7 vol% H_2. All of the results above were, however, obtained with different conditions of preparation such as method of spray, reactor dimension, residence time and initial concentrations of reactants, which made direct comparison among them not reasonable.

We investigated effect of the environment gas on properties of the particles prepared by ultrasonic spray pyrolysis from aqueous solution of silver and copper nitrates under uniquely controlled conditions. The particle properties of interest were its size, morphology, chemical phase and crystallite size of the particles. We finally compared those with the results of the particles prepared from nickel nitrate under the same condition of preparation [13].

EXPERIMENTAL

1. Preparation of Particles

The apparatus for preparation of the particles by ultrasonic spray pyrolysis consisted of ultrasonic atomizer, hot wall tubular reactor heated by a single-zone heating furnace, filter and acid gas absorber, as described elsewhere [8,9,11]. Aqueous solutions of 0.5 M either $AgNO_3$ or $Cu(NO_3)_2 \cdot 3H_2O$ maintained at 30 °C were ultrasonically atomized at a rate of 15 mL/h, and the droplets were carried by nitrogen, air (99.99%) or 90 vol%N_2-10 vol%H_2 at 1 L/min (reference flow rate) to the electrically heated horizontal tubular reactor, 700 mm long with the diameter of 30 mm, maintained at 1,000 °C (reference temperature). Reference residence time was calculated as 25.4 s based on the inlet gas flow rate of 1 L/min at 1 bar and 25 °C. The particles exiting from the reactor were collected by a filter. Water and acid vapor formed from the reactor were finally absorbed in caustic solution before exhausting waste gas.

The main process variable was the gas used to carry the droplets. The furnace set temperature and residence time were also varied. Their effect on the size, morphology, chemical purity and crystallinity of the product particles was investigated. Here, the residence time varied by changing carrier gas flow rate.

2. Characterization of Particles

Size and shape of the particles prepared were observed with scanning electron microscope (SEM, Philips Co, Philips 515) and transmission electron microscope (TEM, Carl Zeiss-EM912 Omega). Number average diameters of the particles were obtained by measuring at least 100 particles shown in SEM images of each sample. Crystallinity of the particles was observed with X-ray Diffractometer (XRD, Scintag-SDS 2000) and the TEM. The crystallite size of the particles was calculated by Scherrer equation. Bulk chemical purity was investigated with the XRD and energy dispersive spectroscope (EDS, Model: Voyager, Noran).

†To whom correspondence should be addressed.
E-mail: sgkim@cau.ac.kr

RESULTS AND DISCUSSION

1. Conversion of Silver Nitrate

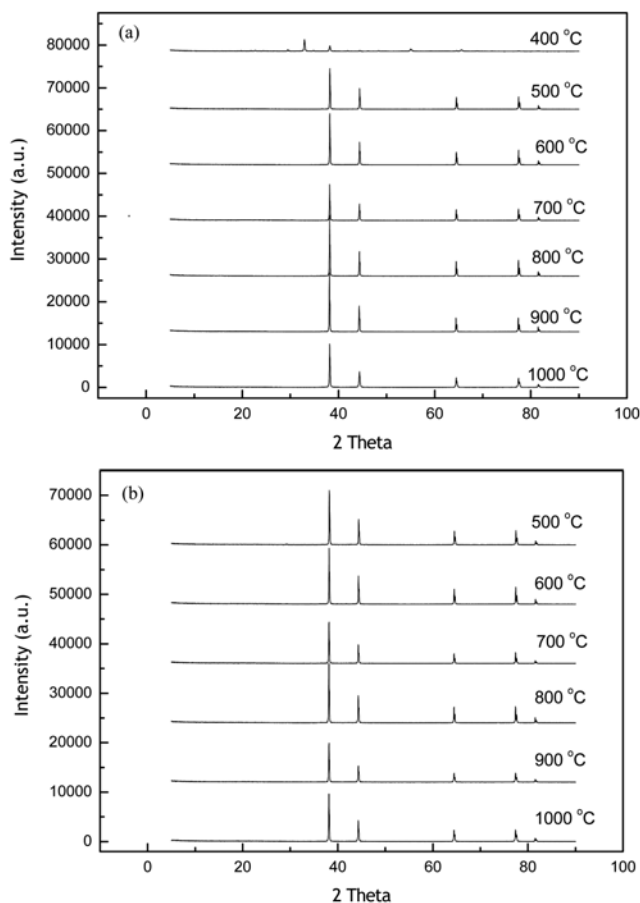XRD patterns of the particles prepared from $AgNO_3$ at different

Fig. 1. XRD patterns of particles prepared at different furnace temperatures under (a) N_2 and (b) air environments, otherwise under reference condition.
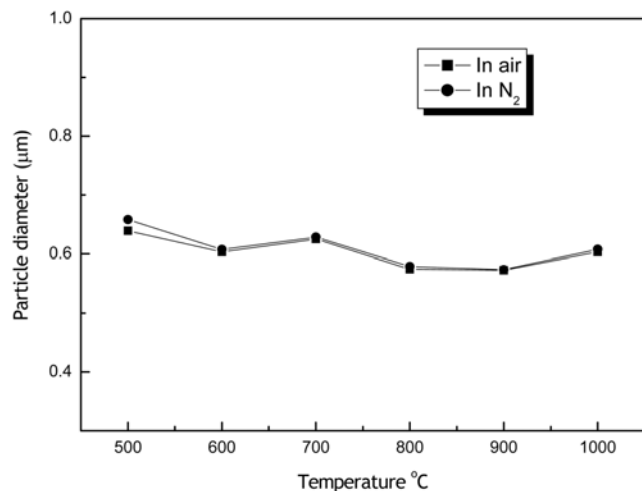
temperatures of preparation under nitrogen [11] could not be differentiated from those under air in locations and heights of all the corresponding peaks, as shown in Fig. 1. Both particles were in the mixed phases of silver nitrate, silver oxide and silver until 400 ℃ and became phase-pure silver at a temperature between 400 ℃ and 500 ℃. The results were different from those of Pluym et al. [10], who reported the minimum temperatures for complete reduction were 600 ℃ and 900 ℃ with nitrogen and air, respectively, as described before. Their residence time of about 68 s, based on the inlet condition which was longer than ours, would have lowered the minimum temperature. The source for such difference is not clear at the moment.

The silver particles became spherical with a smooth surface around 500 ℃ [11], irrespective of the gas used. Fig. 2 shows the number mean diameter of the particles vs. furnace set temperatures for both nitrogen and air. No significant difference was observed in the sizes of the particles prepared from the different gas environments. The particle size tended to slightly decrease with the increase in the furnace set temperature due to densification caused by sintering. But the range of the size variation was within only 30 nm. This suggested that the sintering within each silver particle was so fast that it finished as soon as the reduction to the metallic silver completed. Such high sintering property of the silver was already predicted by Ichinose et al. [15], who estimated the sintering of 20 nm-silver nanoparticles began at 60 ℃ to 80 ℃.

Fig. 3 shows variation in the silver crystallite size for the particles prepared under both nitrogen and air with respect to the furnace set temperature. The sizes of all the crystallites in the particles were around 50 nm, which were not noticeably affected by either the furnace set temperature or gas environment.

Fig. 4 shows SEM images of the particles prepared at 500 ℃ by varying residence time in the reactor. From the figure, irrespective of the gas environments, the increase in the residence time from 12.7 s to 50.8 s, the particles became more spherical with smoother surface, while its decrease to 12.7 s resulted in irregularly shaped particles. Fig. 5 showed XRD patterns of the particles under so pre-
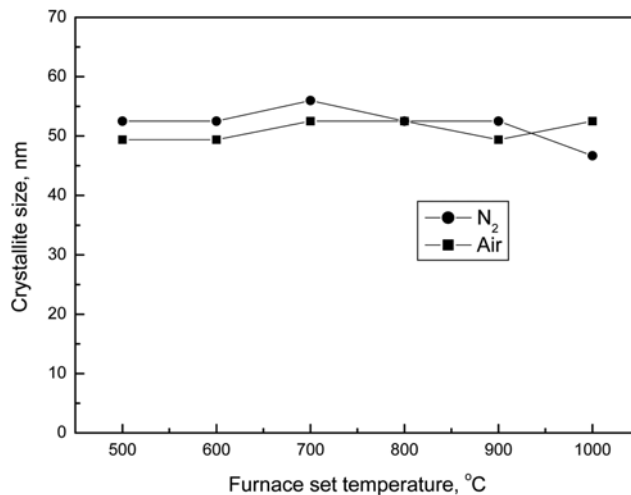

Fig. 2. Number mean diameter of the particles prepared from Ag NO$_3$ with nitrogen and air at different furnace set temperatures, otherwise under reference condition.

Fig. 3. Variation of crystallite size of the particles prepared from AgNO$_3$ with nitrogen and air with respect to furnace set temperature otherwise under reference condition.
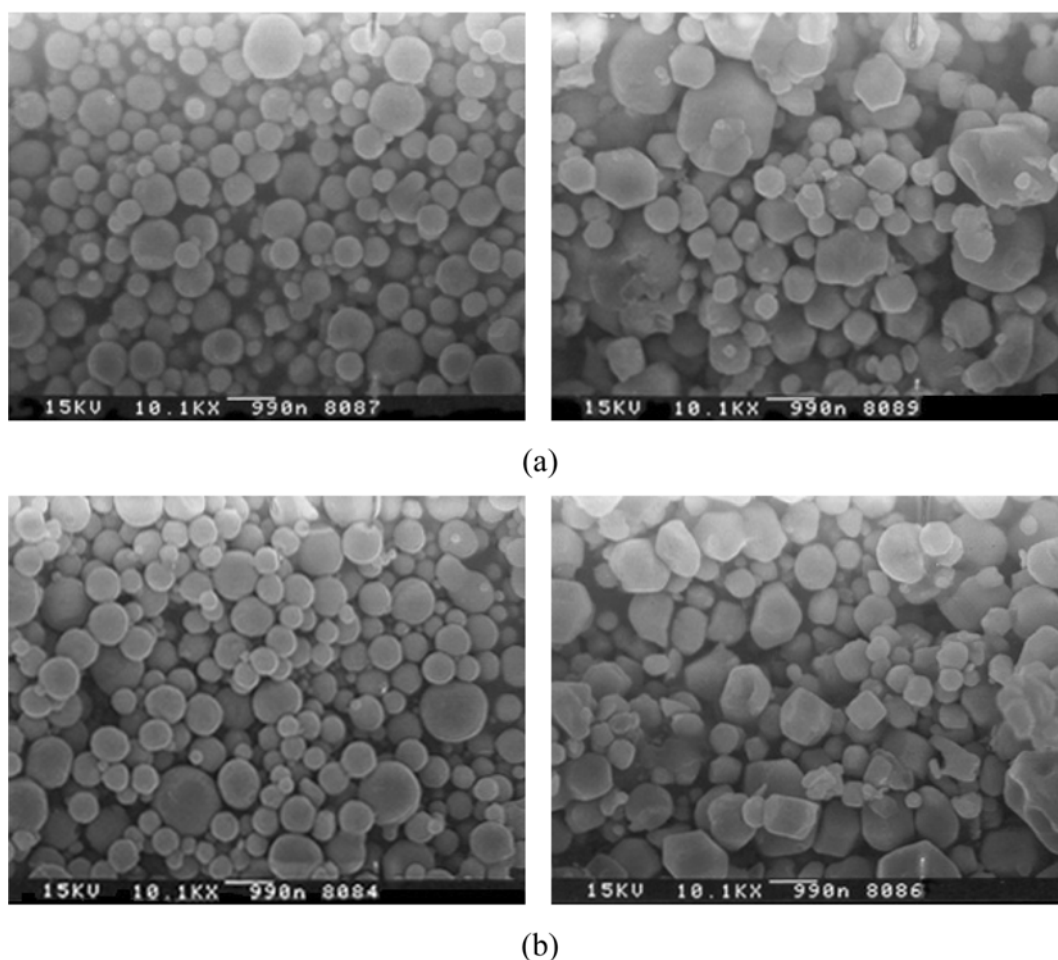
Fig. 4. SEM images of the particles prepared from AgNO₃ with nitrogen and air at difference residence time, otherwise under reference condition. (a) Nitrogen; (L) 50.8 s; (R) 12.7 s; (b) Air; (L) 50.8 s; (R) 12.7 s.
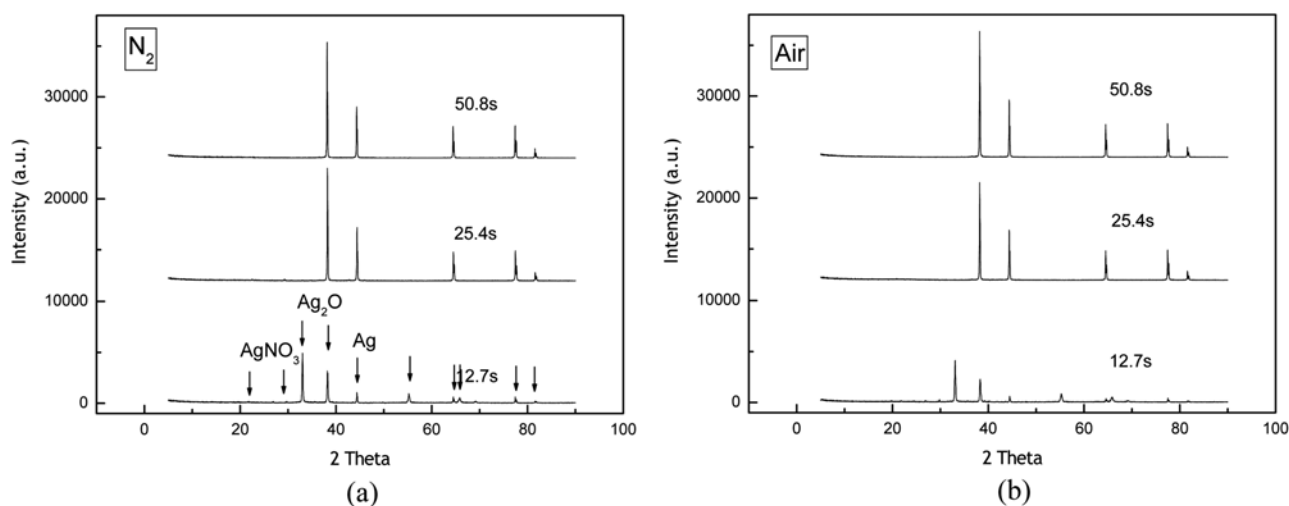

Fig. 5. XRD patterns of the particles prepared from AgNO₃ with (a) nitrogen and (b) air at 500 °C and different residence times in the reactor, otherwise under reference condition.

pared at 500 °C. They were again all the same in the location and height of each peak, irrespective of the gas environment used. The particles prepared at 25.4 s and 50.8 s were all phase-pure silver.

However, the particles prepared at 12.7 s were composed of AgNO₃, Ag₂O and Ag.

In case of silver, its reductivity and sinterability were so high that

E. K. Park et al.

the variation in the environment of gas used could not affect either metallization of the precursor salt, or subsequent sintering and crystallization of metallic silver crystallites within each particle. There-fore, it did not result in any difference in the size and morphology of the particles, and the size of the crystallites, either.
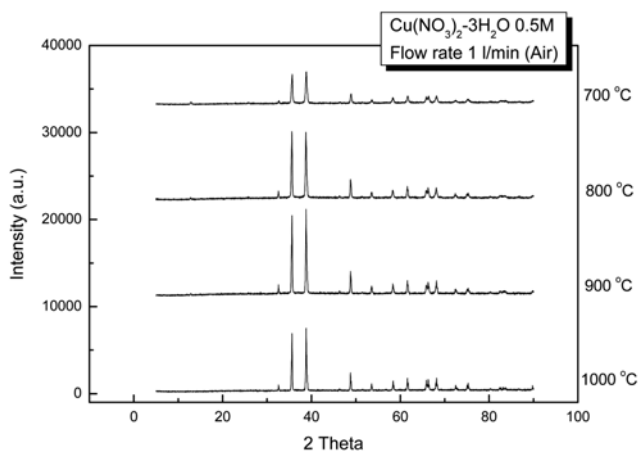

Fig. 6. XRD patterns of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ with air at different furnace set temperatures, otherwise under reference condition.
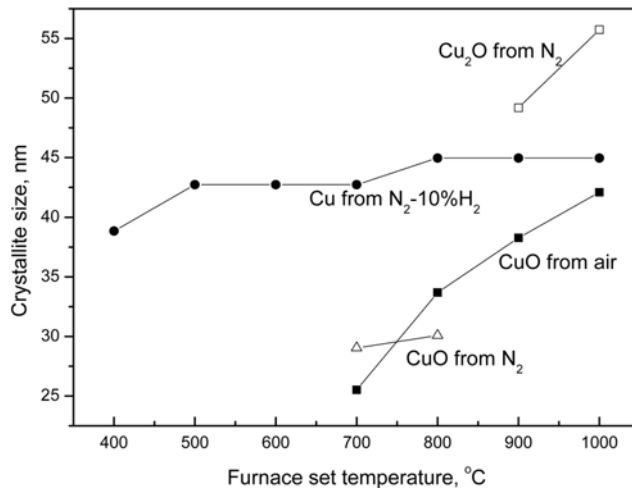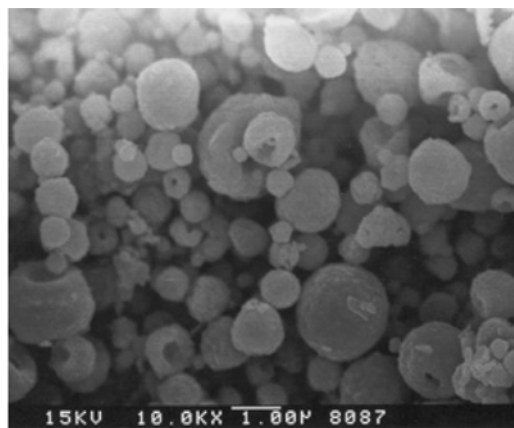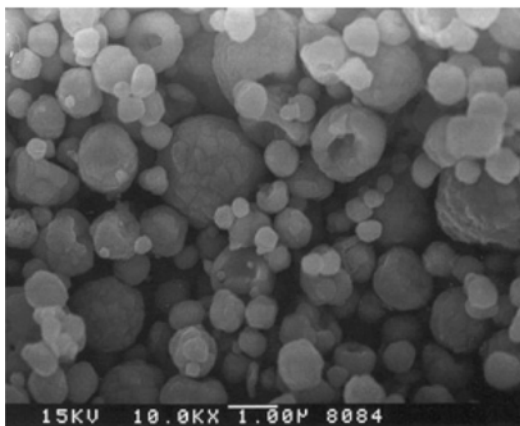

Fig. 7. Effect of furnace set temperature on the crystallite size of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ with different gas environments, otherwise under reference condition.
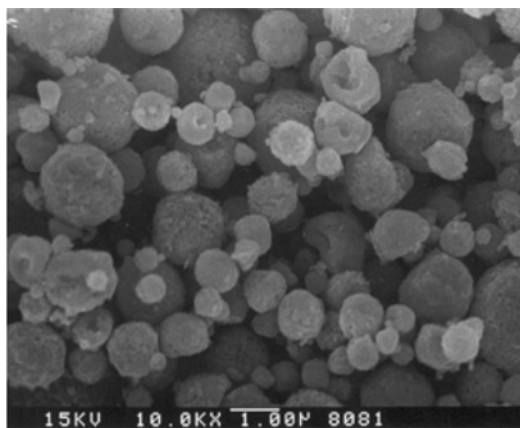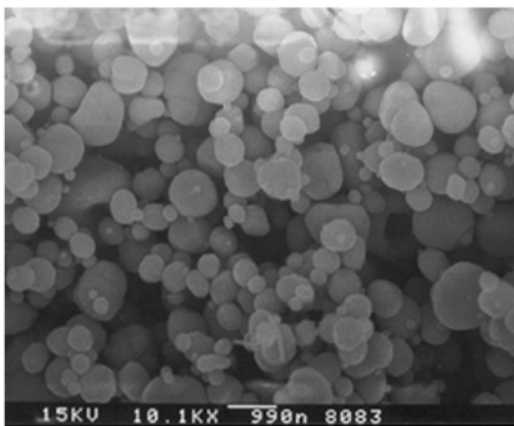

(a)

(b)

(c)

(d)

Fig. 8. SEM images of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ with air at different furnace set temperatures. (a) 700 ℃; (b) 800 ℃; (c) 900 ℃; (d) 1,000 ℃.

2. Conversion of Copper Nitrate

Fig. 6 shows XRD patterns of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ under air environment at different temperatures above 700 °C. It was noted that all the particles were Cu(II)O.

Fig. 7 shows variation in the size of such Cu(II)O crystallites with respect to the furnace set temperature. The figure also contains the plots for the particles prepared under other gas environments to be discussed later. As shown in the figure, the crystallites of the cupric oxide obtained in air monotonically grew as the furnace set temperature increased. Even at 1,000 °C, the crystal growth still kept on increasing.

Fig. 8 shows SEM images of such particles. The Cu(II)O particles prepared at 700 °C were composed of nanocrystallites with rough surface even though they were confined in spheres. Such morphology was typical for the oxide particles just converted from their corresponding salt droplets. Above 700 °C, densification through sintering proceeded within each Cu(II)O particle, leaving a hole-like crater on its smoothened surface to imply that the particles before the sintering had been hollow. Since the particles were not so spherical even at 1,000 °C, the sintering still continued, as well as crystallite growth.

Fig. 9 shows XRD patterns of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ at different furnace set temperatures by replacing air with nitrogen. Such change in the gas environment showed interesting results. While phase-pure Cu(II)O was still obtained at 700 °C, the less oxidized phase Cu_2O appeared at the expense of CuO at 800 °C and finally phase-pure Cu_2O was obtained at 900 °C and up. Majumdar et al. [14] obtained the Cu_2O particles at 800 °C from a 6-jet col-
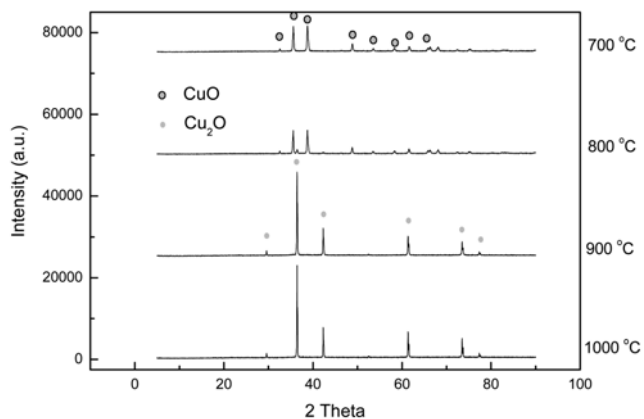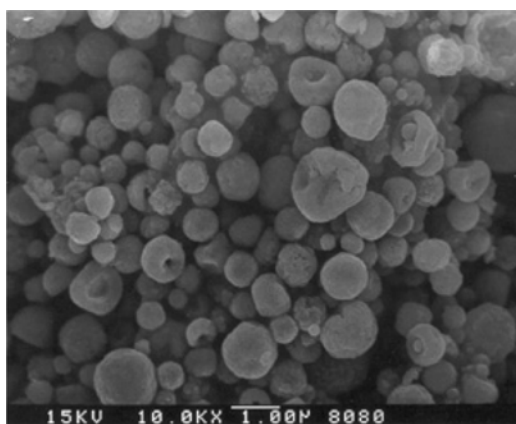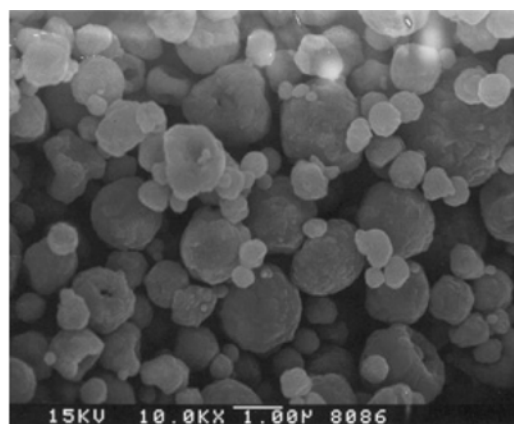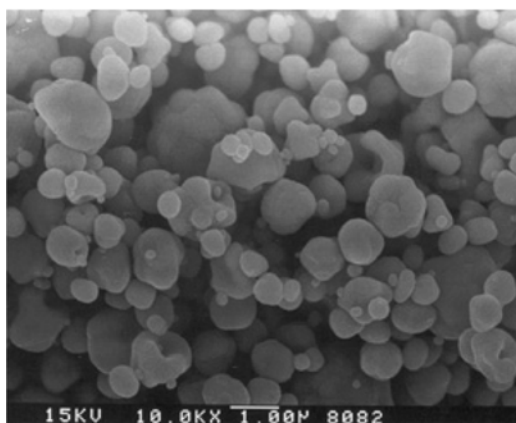

Fig. 9. XRD patterns of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ with nitrogen at different temperatures, otherwise under reference condition.
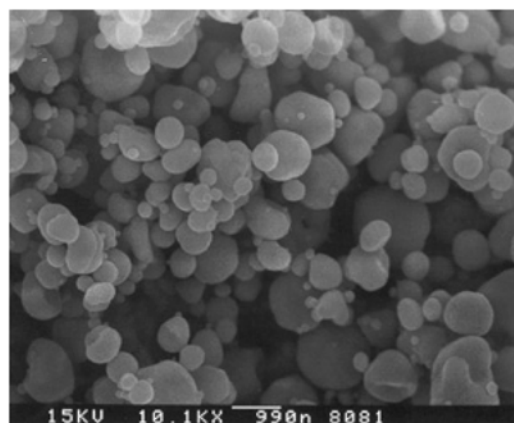

(a)

(b)

(c)

(d)

Fig. 10. SEM images of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ with nitrogen at different temperatures, otherwise under reference condition. (a) 700 °C; (b) 800 °C; (c) 900 °C; (d) 1,000 °C.

E. K. Park et al.

lision aerosol generator but as high as 1,200 °C from ultrasonic generator. They explained such high temperature was required by the increased mass concentration of the droplets generated from the latter compared to the former. Since the mass rate and concentration of droplets, and residence time were not reported in theirs, the reason why the temperature was lowered in our experiment was not clear at the moment.

Although the crystallite size of the cupric oxide in the particles prepared in nitrogen at 700 °C was larger than that prepared under air environment at the same temperature, further growth of the former crystallites was suppressed by the appearance of Cu_2O phase at 800 °C. However, the crystallite sizes of phase-pure Cu_2O particles prepared at 900 °C and 1000°C in nitrogen considerably increased to as high as 49 and 56 nm, respectively, reflecting the crystallization was accordingly facilitated by forming the cuprous oxide.

The particles prepared under N_2 environment at 700 °C had quite different morphologies from those obtained under air environment at the same temperature, as shown in Fig. 10. The crystallites were found more sintered in the former than the latter. However, the particles prepared with nitrogen at 800 °C became unstable, large and irregular with rough surface compared to those at 700 °C, since they were, as described above, in the transition from CuO phase to Cu_2O. Once transformed to the phase-pure cuprous oxide, the particles
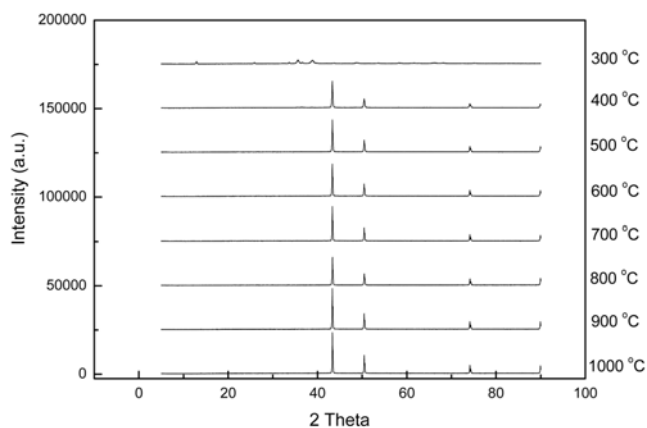

Fig. 11. XRD patterns of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ with 90 vol%N_2-10 vol%H_2 at different temperatures, otherwise under reference condition.

were observed with smoothened surface implying sintering was on-going.

XRD patterns of the particles prepared with N_2-H_2 mixture at different furnace set temperatures are shown in Fig. 11. The particles prepared were all metallic copper except those at 300 °C, which were
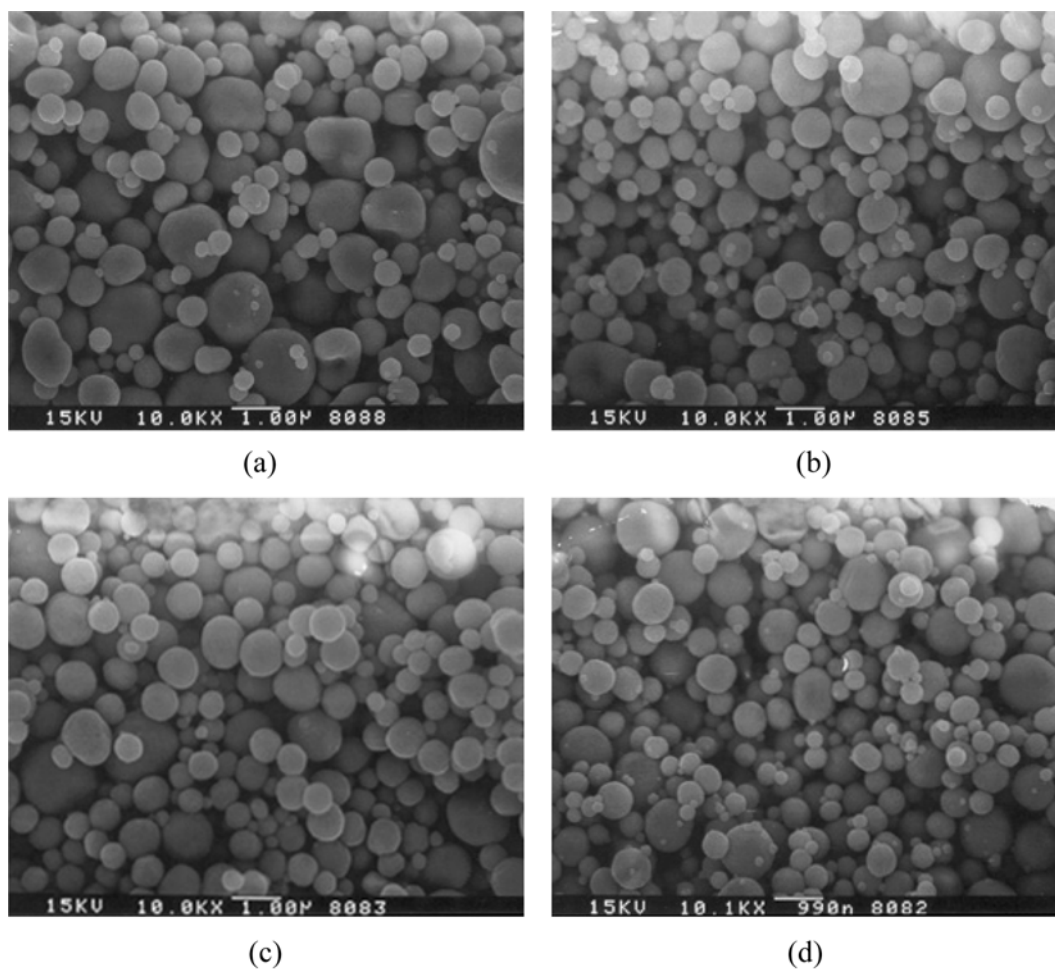

Fig. 12. SEM images of the particles prepared from $Cu(NO_3)_2 \cdot 3H_2O$ with 90 vol%N_2-10 vol%H_2 at different temperatures, otherwise under reference condition. (a) 700 °C; (b) 800 °C; (c) 900 °C; (d) 1,000 °C.
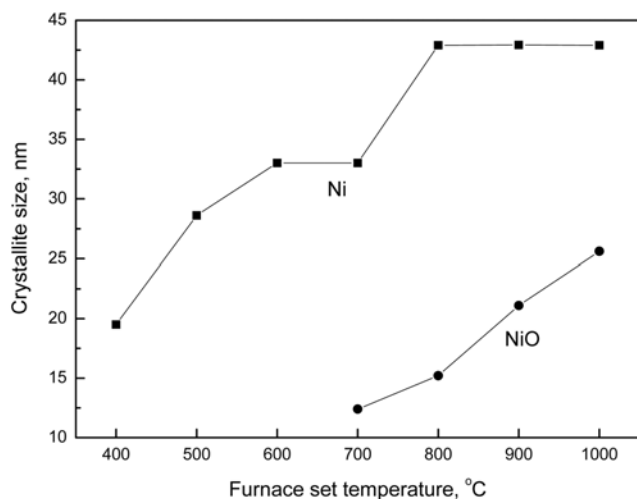
Fig. 13. Variation of crystallite size of the nickel oxide and nickel particles prepared from Ni(NO$_3$)$_2$·6H$_2$O with nitrogen and N$_2$-10 vol%H$_2$ at different furnace set temperatures, otherwise under reference condition.

phase-pure CuO. Thus, with the hydrogen environment, the mid-reduced Cu$_2$O were not found, at least for the temperatures under investigation. The minimum temperature required for preparing phase-pure metallic copper was at most 400 °C. This temperature was even lower than that for silver (~500 °C), which was, however, obtained in nitrogen, and lower than that for metallic nickel (500 °C) in the same hydrogen environment [9]. Such sequence again coincided with the ionization sequence of the metals. As shown in Fig. 7, the crystallite size of the copper particles increased from 39 nm to 43 nm as the temperature increased from 400 °C and 500 °C, while it increased only to 45 nm as the temperature increased from 500 °C to 1,000 °C. Fig. 12 shows SEM images of the particles prepared at temperatures between 700 °C and 1,000 °C with N$_2$-H$_2$ mixture. All the particles shown had smooth surface, and their sphericity and solidness improved with the increase in the temperature.

In case of Ni(NO$_3$)$_2$·6H$_2$O, less reducible than the copper nitrate, the particles obtained even with nitrogen remained as all phase-pure nickel oxide, fully oxidized form, at temperatures of 700 °C and up [13]. Fig. 13 shows sizes of NiO crystallites in the particles prepared from Ni(NO$_3$)$_2$·6H$_2$O with nitrogen at different furnace-set temperatures. The figure also contains those of nickel particles obtained with N$_2$-10 vol% H$_2$ to be described later. The crystallite sizes of nickel oxide were very small compared to the corresponding cupric oxide particles as shown in Fig. 7. They increased from 12 nm only to 25 nm as the temperature increased from 700 °C to 1,000 °C. This reflects the very low sinterability of the nickel oxide crystallites, as described by Che et al. [7]. Thus, the more reducible copper ion easily converted to the state of less oxidation, while the less reducible nickel ions would keep their fully oxidized state.

As shown in Fig. 13, the nickel crystallites grew continuously from 29 to 43 nm as the temperature increased from 500 °C to 800 °C. Thus, it was concluded that for the crystallization as well as the conversion to metal, the copper nitrate was between the silver nitrate and the nickel nitrate.

CONCLUSIONS

The effect of the environment gas on the properties of the particles prepared by spray pyrolysis of the three metallic nitrates such as silver, copper and nickel nitrates was investigated. Silver nitrate, which is the most reducible of them, was easily reduced to metallic silver by spray pyrolysis under nitrogen and even air without any reducing gas. The oxide form of the silver was only observed at temperatures below 500 °C. Furthermore, the chemical composition, size and morphology of the particles and the size of the crystallites were all the same, irrespective of the gas environment, when the furnace set temperature and residence time were fixed. On the other hand, while copper nitrate all converted to phase-pure cupric oxide with air at temperatures between 700 °C and 1,000 °C, with nitrogen the oxide was obtained below 800 °C but converted to cuprous oxide above 800 °C. The sintering and crystallization of the oxide crystallites proceeded with the temperature. The nitrate completely converted to phase-pure copper at 400 °C and up with N$_2$-H$_2$ mixture gas. The rates of the sintering and crystallization of the copper crystallites were lower than those of the silver but higher than those of the nickel.

ACKNOWLEDGMENTS

REFERENCES

1. http://www.silverinstitute.org/, the Silver Institute, 45-55 (2004).
2. T. Addona, P. Auger, C. Celik and G. Chen, *Nickel and copper powders for high capacitance MLCC manufacture*, Passive Component Industry, Nov./Dec., 14-24 (1999).
3. T. T. Kodas and M. J. Hampden-Smith, *Aerosol processing of materials*, Wiley-VCH, 299-306 (1999).
4. T. T. Kodas, M. J. Hampden-Smith, J. Caruso, D. J. Skamser, Q. H. Powell and C. D. Chandler, *Nickel powders, methods for producing powders and devices fabricated from same*, U.S. Patent, 6316100 (2001).
5. K. Nagashima, M. Wada and A. Kato, *J. Mater. Res.*, **5**, 2828 (1990).
6. S. Stovic, I. Ilic and D. Uskokovic, *Mater. Lett.*, **24**, 369 (1995).
7. S. L. Che, K. Takada, K. Takashima, O. Sakurai, K. Shinozaki and N. Mizutani, *J. Mater. Sci*., **34**, 1313 (1999).
8. D. J. Kang, S. G. Kim and H. S. Kim, *J. Mater. Sci.*, **39**, 5719 (2004).
9. K. N. Kim and S. G. Kim, *Powder Technol.*, **145**, 155 (2004).
10. T. C. Pluym, Q. H. Powell, A. S. Gurav, T. L. Ward, T. T. Kodas, L. M. Wang and H. D. Glickman, *J. Aerosol Sci.*, **24**, 383 (1993).
11. S. Y. Yang and S. G. Kim, *Powder Technol.*, **146**, 185 (2004).
12. I. W. Lenggoro, Y. Itoh, N. Iida and K. Okuyama, *Mater. Res. Bull*., **38**, 1819 (2003).
13. D. J. Kang, Ph.D. Dissertation, Chung Ang University, Seoul (2003).
14. D. Majumdar, T. A. Shefelbine and T. T. Kodas, *J. Mater. Res.*, **11**, 2861 (1998).
15. N. Ichinose, Y. Osaki and S. Kashu, Introduction to Ultrafine Particle Technology (in Jap), Ohm Co, 29 (1988).