The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Manufacture of Ultra Fine CuO Powder from Waste Copper Chloride Solution by Spray Pyrolysis Process

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The main purpose of this study is to generate a fine copper oxide powder of high purity, with a compact structure and a uniform particle size by a spray pyrolysis process. The raw material is a waste copper chloride solution formed in the manufacturing process of Print Circuit Board (PCB). This study also examines the influences of various factors on the properties of the generated powder. These factors include the reaction temperature, the inflow speed of the raw material solution, the inflow speed of the air, the size of the nozzle tip, and the concentration of the raw material solution.

It is discovered that, as the reaction temperature increases from 800℃ to 1000 ℃, the particle size of the generated powder increases accordingly, and that the structure of the powder becomes much more compact. When the reaction temperature is 1000℃, the particle size of the generated powder increases as the concentration of copper in the raw material solution increases to 40g/l, decreases as the concentration increases up to 120g/l, and increases again as the concentration reaches 200g/l. In the case of a lower concentration of the raw material solution, the generated powder appears largely in the form of CuO. As the concentration increases, however, the powder appears largely in the form of CuCl. When the concentration of copper in the raw material solution is 120g/l, the particle size of the generated powder increases as the inflow speed of the raw material solution increases. When the concentration of copper in the raw material solution is 120g/l, there is no evident change in the particle size of the generated powder as the size of the nozzle tip and the air pressure increases. When the concentration is 40g/l, however, the particle size keeps increasing until the air pressure increases to 0.5kg/㎠, but decreases remarkably as the air pressure exceeds 0.5kg/㎠

Keywords : spray pyrolysis, waste copper chloride solution, powder, particle size

1. Introduction

Spray pyrolysis[1-3] is a method of solidification through pyrolysis reaction. In this reaction, chemical components are uniformly blended in the solution state so as to make a compound solution, which is in turn sprayed into a reaction oven with high temperature to form fine powders. The advantages of this method include the following: 1) processes such as the mixing, calcination, and milling of solid powder can be omitted, which therefore makes the whole process relatively simple; 2) mixing with impurities can be reduced, and the properties of the generated particles can be controled with respect to the different conditions of the pyrolysis reaction. Using this method, powders with a compact structure, uniform shape, and average diameter smaller than 1㎛ can be generated and the cohesion of particles can be largely avoided. Since the powders can be generated directly, this method is also appropriate for manufacturing metal oxide powder with high functionality. Presently, several companies, such as Scimarec of Japan, Merck of German, and SSC of USA, are producing highly functional ceramic powders manufactured using the spray pyrolysis method. Meanwhile, interest has been shown in the manufacturing of ultra fine metal oxide powders using the spray pyrolysis method[4-6]. The applications of the spray pyrolysis method are expanding quickly. Domestic applications can be found in Pohang Steel and Dongbu Steel, where the waste acid solution that is generated in the process of rinsing the surface of mild steel sheets with hydrochloric acid solution is used as the raw material to generate Fe_2O_3. Except for this steel oxide, however, the spray pyrolysis method is still not used domestically for manufacturing other oxides, especially copper oxide.

The main purpose of this study is to generate a fine copper oxide of high purity, with a compact structure and a uniform particle size (the average particle size is smaller than 1㎛). The powder is generated through a spray pyrolysis process, the raw material of which is a waste copper chloride solution formed in the manufacturing process of Print Circuit Board (PCB). This study also examines the influences of various factors on the properties of the generated powder. These factors include the reaction temperature, the inflow speed of the raw material solution, the inflow speed of the environmental gas and air, the size of the nozzle tip, and the concentration of the raw material solution.

2. Experiment

The waste copper chloride solution generated in the manufacturing process of PCB is used as the raw material in this study. Generally, the concentration of copper in this solution is about 120g/l. By condensation or dilution with distilled water, the final concentrations of copper in the raw material solution can be adjusted to 200, 120, 40, 25, or 12g/l.

In order to generate an ultra fine solid powder with uniform particle size and shape, an efficient spray pyrolysis system was specially designed and built for this study. This system enables the following: the raw material solution can be sprayed into the reaction furnace after being efficiently micronized, the pyrolysis reaction can be completed perfectly, the generated powder can be collected effectively by powder collection devices, such as cyclones and bag filters, and the toxic gases generated in the process can also be cleansed. The schematic diagram of this system is shown in Fig.1[6]. A nozzle with a changeable inside diameter (0.5, 1, 2, 3 and 5mm) is used as the micronization device for this system. By changing the inside diameter of the nozzle, the size of the micronized liquid drop can be controled. Hence, the properties of the generated solid powder can also be controled. In the experiment, the raw material solution was fed through one inlet of the nozzle with inflow speeds of 2~40cc/min, and pressurized air, with pressure of 0.1~3kg/cm2, was fed through the other inlet of the nozzle so that the raw material solution can be micronized. The micronized solution then underwent pyrolysis in the reaction oven with internal temperatures of 800~1100℃. Given various conditions of reaction, an ultra fine powder with diverse physical and chemical properties was generated. In addition, analyses of the particle size and shape using a Scanning Electron Microscope (SEM) and the analysis of the product phase using XRD were performed to determine the property changes of the generated powder.

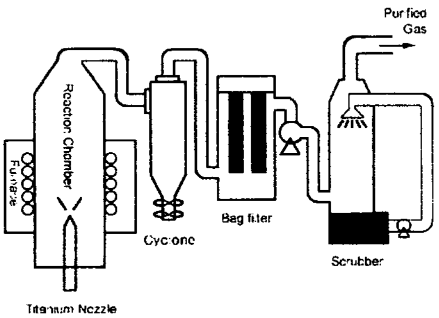


Fig. 1. Schematic diagram of spray pyrolysis system.

3. Results and Discussion

The influence of the reaction temperature on the properties of the powder, which uses waste copper solution as the raw material and is generated through spray pyrolysis process, was investigated first. Fig.2 shows the change of the particle size relative to the increase of the reaction temperature from 800℃ to 1100℃, while the concentration of copper in the raw material solution is kept at 120g/l. It can be seen from this figure that, as the reaction temperature increases, the particle size increases accordingly, and that the structure of the powder becomes much more compact. It is recognized that, because the reaction zone where the pyrolysis reaction occurs is very limited, and the reaction temperature of 800℃ is not sufficient to cause the sintering of the fine solid powder generated through the pyrolysis reaction of the bursted liquid drop, the powder is extremely fine. If the reaction temperature is higher than 900℃, even though the burst of the liquid drop in the pyrolysis reaction is more severe, the particle size of the generated powder still increases because the ultra fine particles become sintered as a result of the high reaction temperature. Consequently, the structure of the powder becomes much more compact. When the reaction temperature is at 800 ℃, the generated powder appears largely in the form of CuCl, and considerably in the form of $CuCl_2.H_2O$. It is believed that the reason why the form $CuCl_2.H_2O$ appears is that the pyrolysis reaction is unable to fully proceed due to the lower reaction temperature and the short reaction time. When the reaction temperature is higher than 900℃, however, all the generated powder appears in the form of CuCl. It is believed that, because of the extremely high concentration of copper (120g/l) in the waste copper solution and the high reaction temperature, there is not a sufficient supply of oxygen in the pyrolysis reaction for generating CuO; hence, the generated powder appears in the form of CuCl.

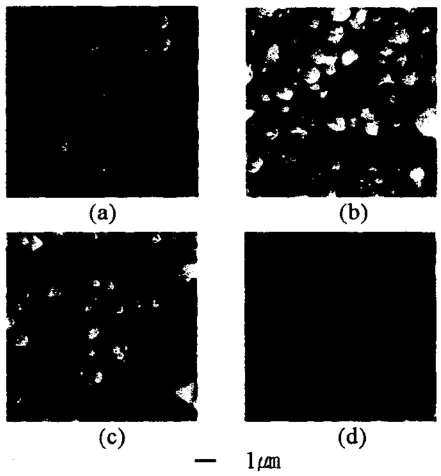


Fig. 2. SEM Photographs of produced powder with reaction temperatures at raw material solution of 120g/ℓ Cu. (a) 800℃ (b) 900℃ (c) 1000℃ (d) 1100℃

Fig.3 shows the structure change of the generated powder relative to the increase of the reaction temperature, when the copper concentration in the waste copper solution is significantly lowered to 25g/l. It can be seen from Fig.3 that the particle size increases as the reaction temperature increases. Until the reaction temperature is 900℃, in contrast to the situation in which the concentration of copper in the waste copper solution is at 120g/l, the particle size of the generated powder appears extremely small, and severe cohesion between particles occurs. While the reaction temperature is higher than 1000℃, the particle size of the powder increases remarkably, and the structure of it becomes more compact. The reason for this is believed to be that a severe burst of the liquid drop does not occur in the case of lower concentrations of the raw material solution. The powder generated at the reaction temperature of 800℃ appears largely in the form of CuCl and $CuCl_2.H_2O$, and partially in the form of CuO. At the reaction temperature of 900 ℃, the powder appears largely in the form of CuCl, while the proportion of CuO increases remarkably. When the reaction temperature increases to 1000℃, the generated powder appears mostly in the form of CuCl, in which the proportion of CuO decreases significantly in contrast to the situation in which the reaction temperature is at 900 ℃. The reason for this is thought to be that the solvent evaporates rapidly in the pyrolysis reaction because of the extremely high reaction temperature. When the reaction temperature increases to 1100℃, the evaporation of solvent becomes more rapid and, as a result, the generated powder appears only in the form of CuCl, and no CuO is generated at all.

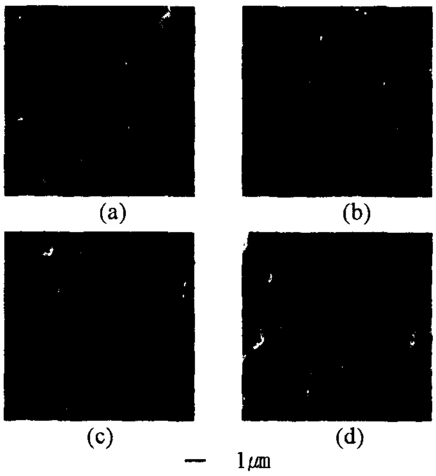


Fig. 3. SEM photographs of produced powder with reaction temperatures at raw material solution of 25g/ℓ Cu.
(a) 800 ℃ (b) 900 ℃ (c) 1000 ℃ (d) 1100 ℃

Fig. 4 shows the property change of the generated powder (revealed by SEM) relative to the concentration of copper in the waste copper solution at the reaction temperature of 1000℃. It can be seen from this figure that the particle size of the generated powder increases significantly as the concentration of copper in the raw material solution increases to 40g/l, decreases as the concentration increases up to 120g/l, and increases again as the concentration reaches 200g/l. While the concentration of copper is at 12g/l, the particle size of the generated powder appears remarkably small, and severe cohesion between particles occurs; this is because of the extremely small size of the liquid drop after the evaporation of the solvent, As the concentration increases up to 40g/l, not only the size of the pyrolyzed liquid drop, but also the particle size of the generated powder increases remarkably because the burst of liquid drop in the pyrolysis reaction is not so severe. As the concentration increases up to 90 and 120g/l, despite the increasing size of pyrolyzed liquid drop, the particle size of the final generated powder decreases as a result of a severe burst of the liquid drop. As the concentration reaches 200g/l, the burst of the liquid drop becomes extremely severe. Nevertheless, because of the extremely large size of the liquid drop resulting from the high concentration of the copper solution, the particle size of the generated powder increases in comparison with the situation in which the concentration is 120g/l. When the concentration of copper is 12g/l, the generated powder appears largely in the form of CuO, and considerably in the form of CuCl. The reason for this is that because of the lower concentration of the solute, the concentration of the solvent inside the liquid drop increases, and therefore the oxygen supply in the pyrolysis reaction increases significantly. As the concentration increases to 25g/l, the generation of CuO diminishes because of the decrease of solvent concentration inside the liquid drop, and the generated powder appears largely in the form of CuCl. As the concentration increases up to 40g/l, almost no CuO is generated, and CuCl is the only form of the powder.

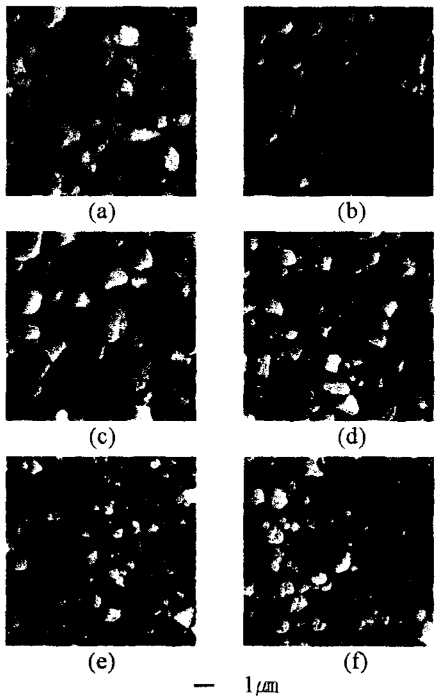


Fig. 4. SEM photographs of produced powder with copper concentration of raw material solution.
(a)12 g/ℓ (b)25 g/ℓ (c)40 g/ℓ (d)90 g/ℓ (e)120 g/ℓ (f)200 g/ℓ

Fig. 5 shows the property change (revealed by SEM) of the powder generated through the pyrolysis reaction relative to the inflow speed of the raw material solution that flows into the reaction oven, given a copper concentration of 120g/l, and a reaction temperature of 1000℃. As the inflow speed increases to 10cc/min, the particle size of the generated powder increases significantly. As the inflow speed increases to 20cc/min, however, there is only a minor increase of the particle size of the generated powder, and the particles appear to be not fully sintered. As the inflow speed of the solution increases up to 40cc/min, the average particle size of the generated powder increases, but the distribution of the particle size appears extremely irregular. Generally, the average size of the liquid drop formed through a two-phase nozzle can be calculated according to the following formula[7]:

$$\chi = 585\frac{\sqrt{\sigma}}{v\sqrt{\sigma}} + \left(\frac{\mu}{v\sqrt{\sigma\rho}}\right)^{0.45}\frac{1000Q_L}{Q_a}^{1.5}$$

where, x is the average particle size, σ is the surface tension of the solution, ρ is the density, υ is the spraying speed μ is the viscosity, Q_L is the amount of solution and Q_a is the amount of air.

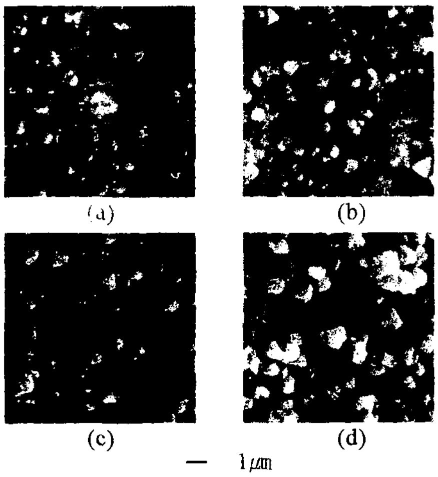


Fig. 5. SEM photographs of powder with inlet speed of solution.
(a) 2cc/min (b) 10cc/min (c) 20cc/min (d) 40cc/min

While the inflow speed is very slow (2cc/min), it is believed that, because the size of the micronized liquid drop decreases, the average particle size of the generated powder becomes extremely small (0.3~0.4㎛), and the structure of the powder therefore becomes considerably compact. As the inflow speed of the solution increases to 10cc/min, even though the size of the liquid drop would increase according to formula (1), because a severe burst of the liquid drop occurs in the process of pyrolysis due to the high concentration of the solution, there is only a minor increase in the average particle size of the finally generated powder. As the inflow speed increases to more than 20cc/min, even though the size of the preliminarily micronized liquid drop becomes considerably large, because the evaporation heat of the solvent released in the process of pyrolysis increases owing to the increase of the inflow speed, the burst of the liquid drop diminishes and in turn the particle size of the generated powder increases further. In contrast to the situation in which the inflow speed is at 10cc/min, however, the generated powder shows an entirely loose (non-compact) structure.

Fig. 6 shows the property change (revealed by SEM) of the powder generated through the pyrolysis reaction relative to the size of the nozzle tip, given a copper concentration of 120g/l and a reaction temperature of 1000℃. As the size of the nozzle tip increases, the average particle size shows a tendency to increase slightly. Compared with the other factors that may influence the properties of the generated powder, however, the influence of the tip size is extremely insignificant. The reason for this is believed to be the combined effect of the following two factors: 1) as the size of the nozzle tip increases, the size of the micronized liquid drop increases, and the particle size of the generated powder increases accordingly; 2) a sever burst of the liquid drop occurs in the process of pyrolysis because of the high concentration of the raw material solution.

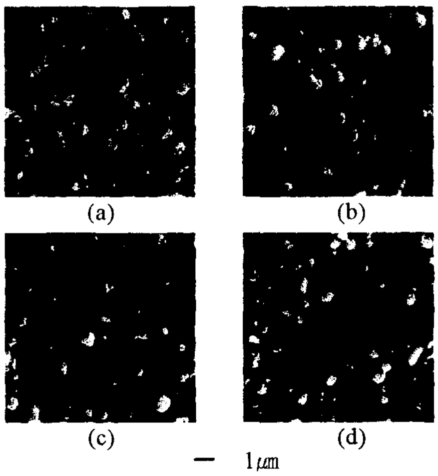
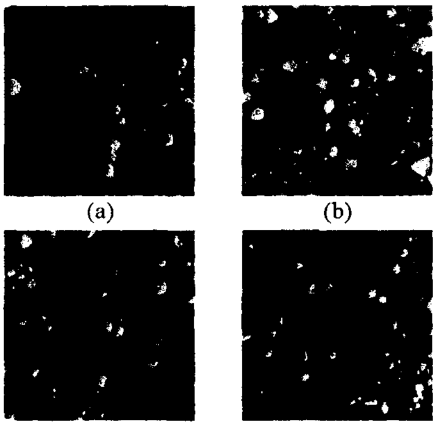


Fig. 6. SEM photographs of powder with nozzle tip size.
(a) 0.5mm (b) 1mm (c) 3mm (d) 5mm

Fig. 7 shows the property change of the generated powder relative to the pressure of the air that flows into the reaction oven, given a copper concentration of 120g/l and a reaction temperature of 1000℃.

With the increase of the air pressure, the average particle size of the powder shows a tendency to decrease slightly. While the air pressure is at 0.1kg/㎠, the distribution of the particle size appears so irregular that powder with a small particle size of 0.2~0.3㎛ and powder with the large particle size of 0.7~0.8㎛ coexist. The reason for this is believed to be that, given an extremely low air pressure, the size of the micronized liquid drop becomes very large and a severe burst of the liquid drop occurs as a result of the extremely high concentration of the solution.

When the air pressure is higher than 0.5kg/㎠, with the increase of the air pressure, the distribution of the particle size becomes more uniform. The reason for this is believed to be that, because the size of the micronized liquid drop decreases due to the increase of the air pressure, a severe burst of the liquid drop does not occur.

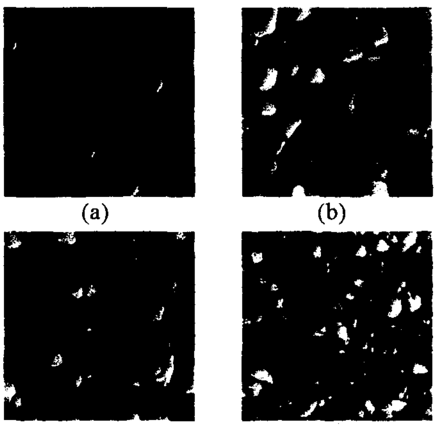


(a) (b) (c) (d)

— 1㎛

Fig. 7. SEM photographs of produced powder with air pressure at raw material solution of 120 g/ℓ Cu.
(a) 0.1kg/㎠ (b) 0.5kg/㎠ (c) 1kg/㎠ (d) 3kg/㎠

When the air pressure is higher than 0.5kg/㎠, with the increase of the air pressure, the distribution of the particle size becomes more uniform. In addition, the form of the generated powder, which is not influenced by the pressure of the air flowing into the reaction oven, is entirely CuCl, and no CuO is generated at all.



(a) (b) (c) (d)

— 1㎛

Fig. 8. SEM photographs of produced powder with air pressure at raw material solution of 40kg/㎠ Cu.
(a) 0.1kg/㎠ (b) 0.5kg/㎠ (c) 1kg/㎠ (d) 3kg/㎠

Fig. 8 shows the property change of the powder generated through the pyrolysis reaction relative to air pressure, given a copper concentration in the raw material solution of 40g/l. Except for the situation in which the air pressure is at 0.1kg/㎠, with the increase of the air pressure, the particle size of the generated powder decreases remarkably, and the distribution of the particle size appears extremely uniform. As the air pressure is lowered to 0.1kg/㎠, the size of the liquid drop increases significantly, and a severe burst of the liquid drop occurs in the process of pyrolysis. As a result, the particle size of the generated powder shows an extremely irregular distribution ranging from 0.3 to 1㎛. As the air pressure increases to 0.5kg/㎠, the severity of the burst of the liquid drop diminishes accordingly. As a result, the average particle size of the generated powder increases to about 1㎛, the distribution of the particle size becomes more uniform, and the structure of the powder becomes more compact. As the air pressure increases to more than 1kg/㎠, the size of the liquid drop and the particle size of the powder decrease significantly because of the remarkably elevated air pressure. While the air pressure is at 3kg/㎠, the generated powder appears partially in the form of CuO. The reason for this is believed to be that, even though the concentration of the solution is not so low as to result in the generation of CuO, contact with oxygen is intensified in the process of pyrolysis as the air pressure increases up to 3kg/㎠ and the form of CuO is generated. Except for the situation in which the air pressure is at 3kg/㎠, the form of the generated powder appears entirely as CuCl, which is not influenced by the pressure of the air that flows into the reaction oven.

4. Conclusion

1) As the reaction temperature increases from 800℃ to 1000℃, the particle size of the powder generated through the process of pyrolysis increases, and the structure of the powder gradually becomes compact. Not influenced by the reaction temperature, the generated powder appears largely in the form of CuCl, and no CuO is generated.

2) When the reaction temperature is 1000℃, the particle size of the powder increases as the concentration of copper in the raw material solution increases up to 40g/l, decreases as the concentration increases up to 120g/l, and increases again as the concentration reaches 200g/l. In the case of a lower concentration of the raw material solution, the generated powder appears in the form of CuO. As the concentration increases, however, the powder appears in the form of CuCl.

3) When the concentration of copper in the raw material solution is 120g/l, the particle size of the generated powder increases as the inflow speed of the raw material solution increases.

4) When the concentration of copper in the raw material solution is 120g/l, there is no evident change of the particle size of the generated powder as the size of nozzle tip increases.

5) When the concentration of copper in the raw material solution is 120g/l and the air pressure is at 3kg/㎠, the generated powder appears extremely fine (the average particle size is about 0.3㎛). With the increase of air pressure, however, there is no evident change of the particle size. When the copper concentration is 40g/l, the particle size increases as the air pressure increases to 0.5kg/㎠, but decreases remarkably as the air pressure exceeds 0.5kg/㎠.

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