Synthesis and Microstructures of Metal Particles Prepared by Spray Pyrolysis

Takayuki Koderu, Kenichi Myoujin and Takashi Ogihara

University of Fukui, 9-1 Bunkyo 3, Fukui-shi, Fukui, 910-8507 Japan

Fax: 81-776-27-8624, e-mail: ogihara@matse.fukui-u.ac.jp

Ag, Ni and Cu spherical fine powders were continuously produced by carrying out an aerosol process in a mass nanopowder production apparatus. The particle size, particle morphology, crystal phases and crystallinity of the as-prepared powders were characterized by SEM and XRD. The particles were nonaggregated and they exhibited a spherical morphology with a narrow size distribution.

Key words: Spray pyrolysis, Metal particles, Silver, Nickel, Copper, Powder production apparatus

1. INTRODUCTION

Recently, spherical metal fine powders have been attracting considerable attention as compounds that can be used in the development of various industrial applications such as alloy steel, magnetic materials, battery, and catalyst. For the development of these industrial applications, metal particles should be spherical, nonaggregated, micron-sized or smaller and should have a homogeneous composition. Fine metal particles have been already prepared by a liquid phase process such as precipitation from solution [1]. However, the particles prepared by this method are typically aggregated, nonuniform, and irregular shaped. Spray pyrolysis [2–5] is a versatile process that is used to synthesize ceramic and metal fine powders. The advantages of spray pyrolysis are that it allows us to control the particle size, particle size distribution, and particle morphology. In addition, fine powders with a homogeneous composition can be easily synthesized,

because the starting solution components are kept in a mist. In this study, the particle characteristics of Ag, Ni and Cu particles synthesized by spray pyrolysis were investigated. We experimented the use of a mass nanopowder production apparatus in the aerosol process (spray pyrolysis). In this process, internal combustion-type furnace with gas burner was used to carry out the thermal decomposition of aerosol. It has been not reported that synthesis technique of spherical Ag, Ni and Cu particles by spray pyrolysis using internal combustion-type furnace was investigated.

2. EXPERIMENTAL

Three types of the starting solutions were prepared to synthesize metal particles. Silver nitrate was used as a silver source. Nickel acetate was used as a nickel source. Copper acetate was used as a copper source. These compounds were dissolved in water at room temperature. The concentration of starting solution ranged from 0.1 to

Fig. 1 Schematic diagram of mass nanopowder production apparatus

Fig. 2 Thermal behavior of the metal salts. (a) $\text{Ag}(\text{NO}_3)_2$, (b) $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, (c) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$

Fig. 3 SEM images of metal particles. (a) Ag particles, (b) Ni particles, (c) Cu particles

1.0 mol/dm^3 .

The schematic diagram of the mass nanopowder production apparatus is shown in Figure 1. This apparatus consists of an aerosol generation unit with nine ultrasonic vibrators, internal combustion-type furnace with six gas burners, and a powder collector with seven bag filters. The thermal decomposition of aerosol was carried out uniformly after it was introduced into the internal combustion-type furnace; this resulted in the formation of as-prepared powders, which were continuously collected by the bag filter. The aqueous metal salts solution was misted at 1.6 MHz using nine ultrasonic vibrators (HM-1630, Honda Electronics) in an aerosol generation unit at $1 \text{ dm}^3/\text{hr}$. Air was used as the carrier gas during the preparation of Ag powders using this apparatus. On the other hand, N_2 was used as the carrier gas during the preparation of Ni and Cu powders using this apparatus. LP gas was used as the gas source. The temperature of the drying zone ranged from 80 to 400°C , and that of the pyrolysis zone ranged from 400 to 600°C . However, the temperature around the gas burner in the internal combustion-type furnace was approximately 800°C . In this study, it was observed that because the thermal decomposition temperatures of $\text{Ag}(\text{NO}_3)_2$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ranged from 100 to 450°C (Figure 2), the temperature of the pyrolysis zone ranged from 400 to 600°C .

The thermal behavior of metal salts and as-prepared powders was observed using TG-DTA (DTG-60,

Shimadzu). The crystal phase of the as-prepared powders was observed by powder X-ray diffraction (XRD, XRD-6100, Shimadzu) using $\text{CuK}\alpha$ radiation. The particle size and morphology of the as-prepared powders were determined by using a scanning electron microscope (SEM, JSM-6390, JEOL). In the SEM images, 200 particles were randomly sampled to determine the average particle size and the geometrical standard deviation (σ_g) of the as-prepared powders. The geometrical standard deviation (σ_g) was defined as equation (1):

$$\sigma_g = x_{84.13} / x_{50}. \quad (1)$$

In Eq. (1), x_{50} is median diameter and $x_{84.13}$ is 84.13% diameter of cumulative particle quantity. The specific surface area (SSA) of the as-prepared powders was measured by a BET method using N_2 adsorption (BELSORP-mini2, BEL JAPAN).

RESULT AND DISCUSSION

The yield of all the as-prepared powders was over 80%. This resulted in a high collecting performance of the filter used in the synthesis of the powders. From TG-DTA analysis, it was found that a few wt% of the undecomposed source salt was contained in all the as-prepared powders.

Figure 3 (a), (b), and (c) show the SEM images of Ag, Ni and Cu particles, respectively. These particles were

Fig. 4 XRD patterns of the as-prepared powders. (a) Ag, (b) Ni, (c) Cu

Fig. 5 Average particle size and geometrical standard deviation (σ_g) as functions of the concentration of the starting solution

nonaggregated and exhibited spherical morphology with a narrow size distribution. The average size of the Ag particles obtained from the nitrate solution was 400 nm when the concentration of the starting solution was 0.1 mol/dm³. The geometrical standard deviation (σ_g) calculated from the particle size distribution was 1.25. When the concentration of the starting solution was 0.1 mol/dm³, the average particle size and the geometrical standard deviation (σ_g) of Ni particles obtained from the carboxylic acid solution was 500 nm and 1.3, respectively. On the other hand, The average particle size and the geometrical standard deviation (σ_g) of Cu particles obtained from the carboxylic acid solution was 400 nm and 1.25, respectively. It was found that the particle size of the as-prepared powders was almost the same as that of the particles obtained when ultrasonic spray pyrolysis was performed in an electric furnace. The SSA of the as-prepared powders was 1.2–1.4 m²/g.

The crystal phases and crystallinity of the as-prepared powders were observed by using the XRD. Figure 4 shows the XRD patterns of the as-prepared powders. From these patterns, it was observed that the diffraction peak of the Ag as-prepared powders was in agreement

with that of silver, and other phases were not observed. The crystallinity of the Ag as-prepared powders was very high. However, the crystal phases of the Ni as-prepared powders were the same as those of nickel and nickel oxide. This suggested that O₂ in the atmosphere was responsible for the oxidation of nickel during pyrolysis, because the internal combustion-type furnace was not sufficiently airtight. On the other hand, the crystal phase of the Cu as-prepared powders was the same as those of copper oxide. When the as-prepared powders were first collected by the bag filter, the as-prepared powders were the red powders. However, the red powders were gradually changed to black powders when the as-prepared powders were continuously collected. This suggested that O₂ in the atmosphere was responsible for the oxidation of copper during collection.

Figure 5 shows the average particle size and the geometrical standard deviation (σ_g) as functions of the concentration of the starting solution. The average particle size increased with increasing the concentration of the starting solution. However, the geometrical standard deviation (σ_g) was independent

of the concentration of the starting solution. This result was similar to that of oxide powders prepared by spray pyrolysis [7, 8].

CONCLUSION

The spherical metal powders were successfully prepared using a mass nanopowder production apparatus by the aerosol process. Using this apparatus ensured a high efficiency of collecting the as-prepared powders. The yield of the powders was over 80 %. The as-prepared powders were nonaggregated and exhibited a spherical morphology with a narrow size distribution. When the concentration of the starting solution was 0.1 mol/dm³, the average particle sizes of the Ag, Ni and CuO particles were 400 nm, 500 nm and 400 nm, respectively. The particle morphology and particle size of the as-prepared powders obtained by using the mass nanopowder production apparatus were almost the same as those of the powders obtained by performing spray pyrolysis in an electric furnace.

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