Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 2617–2623
www.elsevier.com/locate/jeurceramsoc

Droplet size control in the filter expansion aerosol generator

D.S. Jung, Y.C. Kang *

Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

Received 1 October 2007; received in revised form 29 February 2008; accepted 6 March 2008
Available online 29 April 2008

Abstract

A new capability for droplet generation through the filter expansion aerosol generator (FEAG) process has been found. The mean sizes and size distributions of droplets generated by the FEAG process have been estimated from the resulting powders. The mean sizes of the droplets could be controlled from 1.7 to 25 μm. Surface tension and the viscosity of spray solutions controlled by adding polyethylene glycol (PEG) affected the mean sizes of the droplets. The mean sizes of droplets generated at a pressure of 160 Torr changed from 4.3 to 12.1 μm when the concentrations of PEG were changed from 1.6×10^{-4} to 1.6×10^{-3} M. The addition of PEG into the spray solution improved the size distribution of the droplets. The mean sizes of droplets generated from the spray solution with a concentration of 4.8×10^{-4} M PEG changed from 1.7 to 25 μm when the reactor pressures were changed from 60 to 400 Torr. The droplets generated at pressures between 160 and 360 Torr had a narrow size distribution.

Keywords: Powders-gas phase reaction; Traditional ceramics; Powders-chemical preparation

1. Introduction

Spray aerosol generators can be applied in the formation of thin films and the preparation of fine powders by spray pyrolysis.[1–3] Small, uniform-sized droplets are needed for the preparation of ultrafine powders and thin film for integrated circuits with submicron features. For these applications, the droplet size should be around 1 μm and large production rates are required. An ultrasonic spray generator offers a reasonably high production rate and yields droplet diameters on the order of μm. Ultrasonic spray generators have therefore been used for the commercial production of useful ceramic and metal powders.

Kang and Park developed a new liquid aerosol generator named the filter expansion aerosol generator (FEAG).[4] The FEAG process comprised a liquid aerosol generator which produces fine-sized droplets under low pressure. It has been applied to the preparation of advanced ceramic, metal and glass powders.[5–9] The resulting powders have similar characteristics to those prepared by ultrasonic spray pyrolysis.

The required mean size for ceramic, metal, and glass powders used in the electronic industries is becoming smaller and smaller. However, in some application fields, powders with mean sizes between 3 and 10 μm are required. Therefore, droplet generators must be able to generate droplets with mean sizes of several microns and several tens of microns. Pneumatic nozzles have the capability of producing droplets with mean sizes of several tens of microns.[10] On the other hand, the droplets generated by these pneumatic nozzles have a broad size distribution. Electro-spray generators can be used to generate droplets smaller than 2 μm but the production rate of these size droplets is restrictive.[11] Ultrasonic spray generators are also restricted in the generation of droplets smaller than 2 μm or droplets larger than 10 μm.

In this study, a new capacity for droplet generation via the FEAG process was investigated. The mean sizes of the droplets were controlled from micron sized to several tens of microns. The droplet generation characteristics were estimated from the characteristics of aluminum oxide powders. Surface tension and viscosity of the spray solution were controlled by changing the concentrations of polyethylene glycol added to the spray solutions. The pressure of the reactor was changed from 60 to 400 Torr by controlling the capacity of the vacuum pump.

2. Experimental

The schematic diagram of the modified FEAG process used in this study is shown in Fig. 1. The apparatus consists of a

* Corresponding author. Tel.: +82 2 2049 6010; fax: +82 2 458 3504.
E-mail address: yckang@konkuk.ac.kr (Y.C. Kang).

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2008.03.017

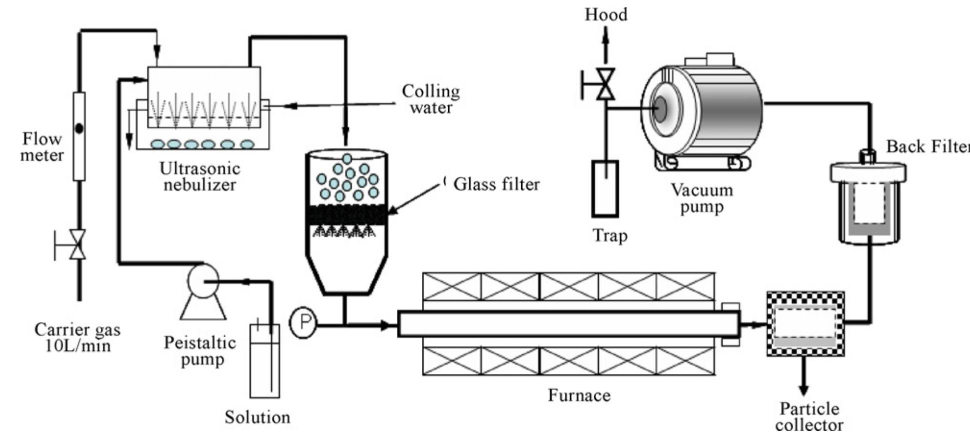

Fig. 1. Schematic diagram of filter expansion aerosol generator (FEAG) for preparing Al_2O_3 powders.

porous glass filter, an ultrasonic spray generator, a vacuum pump and a bag filter. An ultrasonic spray generator was used as a supply system for the spray solution to ensure a continuous, uniform quantity. The detail droplet formation mechanism in the FEAG process has been investigated in previous research.[4] The spray solution was supplied through an ultrasonic spray generator using carrier gas on to a glass filter surface where it formed a thin liquid film. The liquid flows through pores of the glass filter with carrier gas. Liquid flow rate is controlled so as to maintain two phase flow in the pores of the glass filter. At the bottom of the filter, multiple expansion occurs through multiple channels and aerosol stream is formed.

Aluminum oxide powders were prepared from aqueous and polymeric spray solutions using the FEAG process. The aqueous solution was prepared by dissolving aluminum nitrate in distilled water. The concentration of aluminum nitrate was 0.2 M. Polyethylene glycol (PEG 200) was dissolved in the spray solutions to control surface tension and viscosity. The concentration

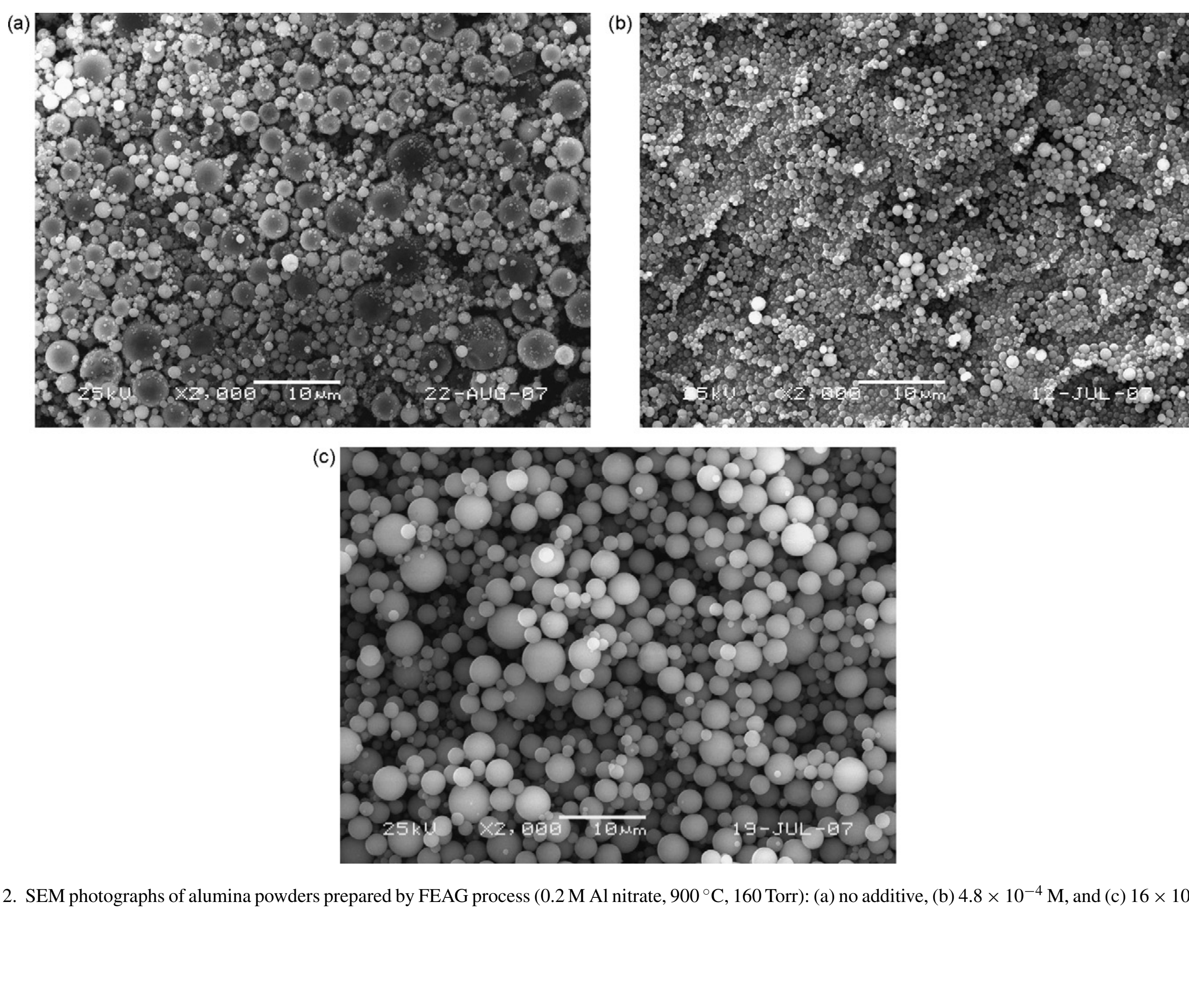

Fig. 2. SEM photographs of alumina powders prepared by FEAG process (0.2 M Al nitrate, 900 °C, 160 Torr): (a) no additive, (b) 4.8×10^{-4} M, and (c) 16×10^{-4} M.

of PEG was changed from 1.6×10^{-4} to 4.8×10^{-3} M. The reactor temperature of the FEAG process was maintained at a temperature of 900 °C. The pressure of the reactor was changed from 60 to 400 Torr by controlling the capacity of the vacuum pump.

The surface tension of spray solutions was measured with a thermostated tensiometer (model K10 Krüss GmbH, Hamburg, Germany), using a platinum–iridium ring and the Du Noüy method. Measurements were taken at a room temperature of 20 °C. The tensiometer was calibrated with distilled water ($\sigma = 72.8\ \mathrm{mN\,m^{-1}}$ at 20 °C). Viscosity measurements were measured using an Ostwald Viscometer immersed in a temperature-controlled water bath in which the temperature was maintained at 20 °C. The Viscometer was calibrated with a sample of distilled water using the published data for the viscosity of water. The thermal properties of the prepared powders were measured using a thermo-analyzer (TG–DSC, Netzsch, STA409C, and Germany) in the temperature range from 40 to 800 °C at a heating rate of 10 °C/min. The mean sizes and size distribution of the powders were investigated by scanning electron microscopy (SEM, JEOL, JSM 6060).

3. Results and discussion

The morphologies of the aluminum oxide powders prepared by the FEAG process from the spray solutions with various concentrations of PEG are shown in Fig. 2. The pressure of the reactor was maintained at 160 Torr. The mean sizes of the powders were affected by the concentrations of PEG added to the spray solutions. The powders obtained from the aqueous spray solution were of large and bimodal size distributions. Low concentration of PEG added to the spray solutions decreased the mean size of the precursor powders. Conversely, the mean size of the precursor powders increased with increase of the concentrations of PEG above 8.1×10^{-4} M. The mean sizes of the powders measured from the SEM photographs are shown in Fig. 3. The mean size of the powders obtained from spray solutions with PEG changed from 0.7 to 2.1 μm when the concentrations of PEG were changed from 1.6×10^{-4} to 1.6×10^{-3} M.

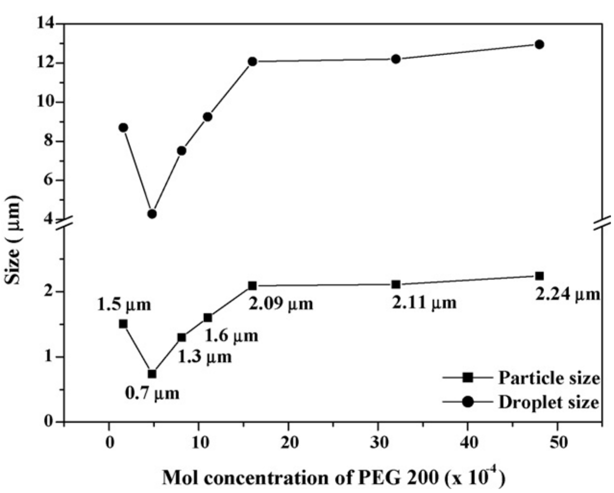

Fig. 3. Powder size and droplet size as a function of the mol concentration of PEG.

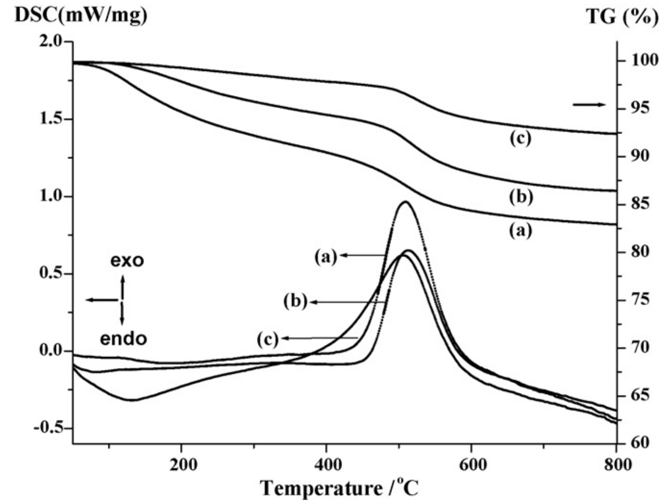

Fig. 4. TG/DSC curves of alumina powders: (a) 4.8×10^{-4} M, (b) 16×10^{-4} M, and (c) 48×10^{-4} M.

The aluminum oxide powders prepared by the FEAG process from the spray solutions with PEG had dense inner structures. The drying of PEG within the droplet formed a highly viscous gel consisting of a three-dimensional polymer network. This viscous gel promoted the volume precipitation of precursors within the droplets and resulted in the formation of powders spherical in shape and with a dense morphology.[12] Fig. 4 shows the TG/DSC curves of the powders prepared by the FEAG process obtained from the spray solutions with low and high concentrations of PEG. In the TG curves, two states of weight loss are observed. The first weight loss occurs at temperatures between 40 and 200 °C, resulting from the removal of adsorbed water in the powders. The weight loss of the powders obtained from the spray solution with a low concentration of PEG was larger than that of the powders obtained from the spray solution with a high concentration of PEG. The second weight loss occurred at temperatures between 400 and 600 °C. In the DSC curves, the powders had exothermic peaks in the temperature range 400–600 °C. These exothermic peaks were accompanied by weight losses corresponding to the decomposition of carbon components. A complete decomposition of the carbon components did not occur because of the short residence time of the powders inside the hot wall reactor. The total weight loss of the powders changed from 8.6 to 5.6 wt.% according to the concentrations of PEG added to the spray solutions. The total weight loss of the powders obtained from the spray solution with a high concentration of PEG was lower than that of the powders obtained from the spray solution with a low concentration of PEG. The carbon impurity of the powders did not increase the mean size of the powders obtained from the spray solution with a high concentration of PEG. Therefore, the change of the mean size of the powders according to the concentrations of PEG added to the spray solutions was caused by the difference of the mean size of droplets generated by the FEAG process. Assuming one dense powder is derived from one droplet, the

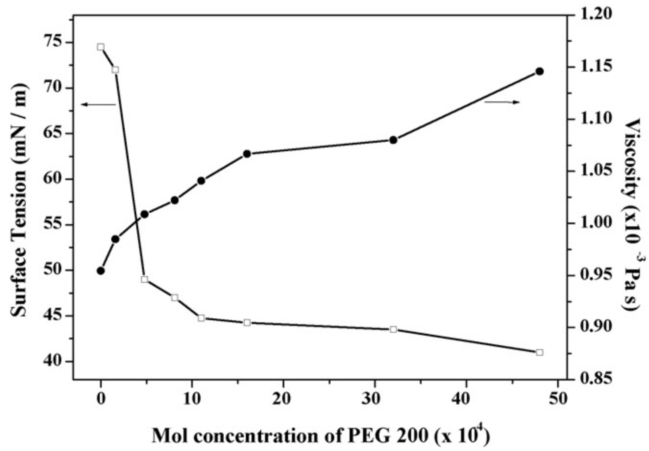

Fig. 5. Surface tension and relative viscosity of spray solutions as a function of the mol concentration of PEG.

mean diameter of droplets can be calculated using the following equation:

$$d_{\text{drop}} = d_{\text{particle}} \times \left(\frac{\rho_x}{M_x \times C \times 10^{-3}} \right)^{1/3} \quad (1)$$

where d_{drop} and d_{powder} are the mean diameter of the droplets and powders, respectively. ρ_x and M_x are the density and molecular weight of oxide or dried salt powders. C is the molar concentration of the salt solution. The mean sizes of the droplets calculated from Eq. (1) are shown in Fig. 3. The mean sizes of the droplets generated by the FEAG process changed from 4.3 to 12.1 μm when the concentrations of PEG changed from 4.8×10^{-4} to 1.6×10^{-3} M.

The mechanism of formation for droplets in the FEAG process is similar to that of a pneumatic nozzle. A thin liquid film and carrier gas pass through the filter pores driven by the carrier gas and expand into a low pressure chamber. The mean sizes of droplets generated by a pneumatic nozzle are strongly affected by the surface tension and the viscosity of the spray solutions.[13] Therefore, the mean sizes of droplets generated by the FEAG process are also affected by the surface tension and the viscosity of the spray solutions. Fig. 5 shows the change of the surface tension and the viscosity of the spray solutions according to the concentrations of PEG added to the spray solutions. A low concentration of PEG added to the spray solution strongly lowered the surface tension of the solution. With further addition of PEG, the surface tensions of the spray solutions

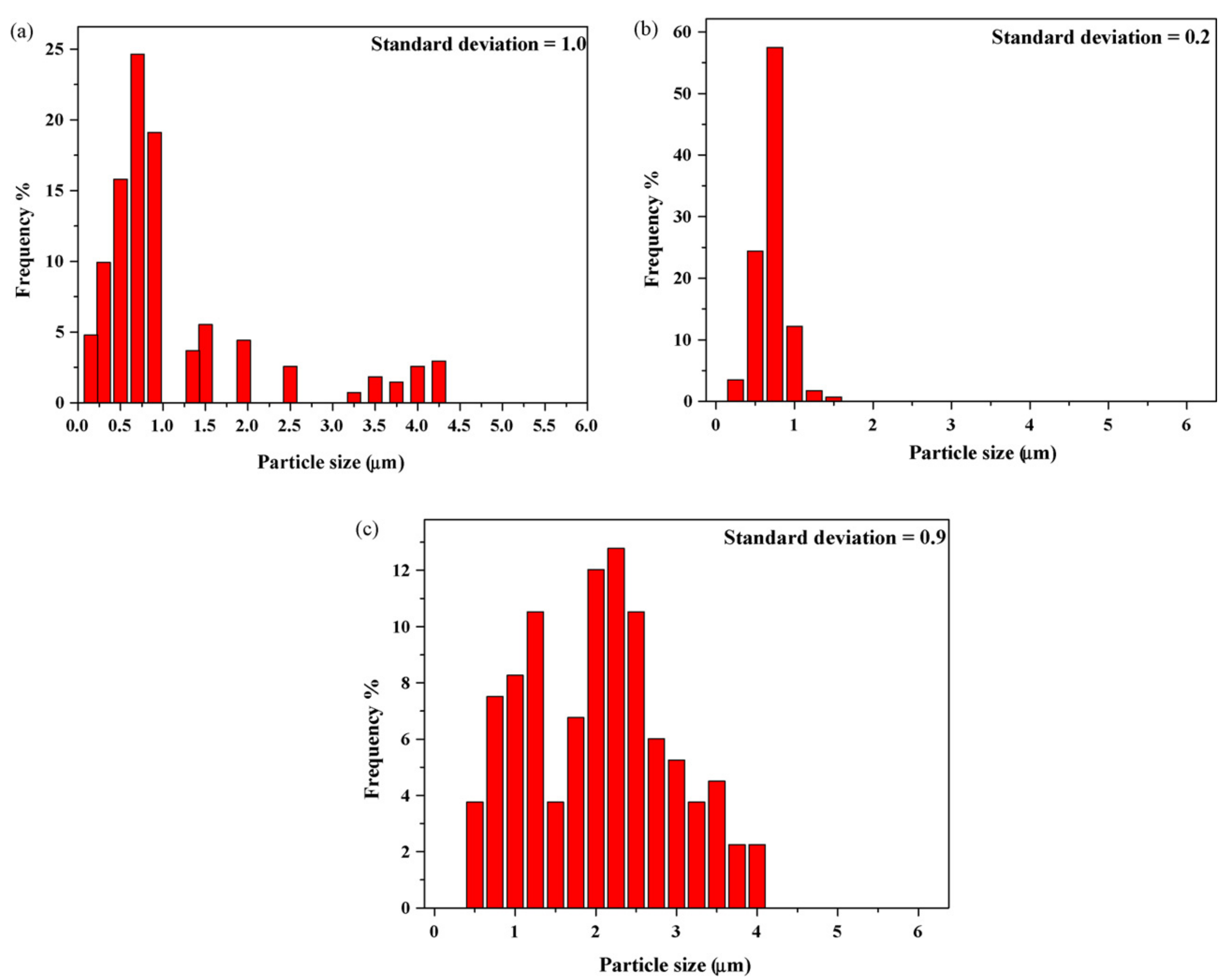

Fig. 6. Size distributions and standard deviations of the prepared alumina powders prepared from spray solution with different mol concentration of organic additive: (a) no additive, (b) 4.8×10^{-4} M, and (c) 16×10^{-4} M.

were much less affected. The viscosities of the spray solutions steadily increased when the concentrations of PEG were raised. The addition of a low concentration of PEG to the spray solution decreased the mean size of droplets by decreasing the surface tension of the spray solution. Conversely, the addition of a high concentration of PEG into the spray solution increased the mean size of droplets by increasing the viscosity of the spray solution. Therefore, the droplets generated at a pressure of 160 Torr had the lowest mean size when the concentration of PEG added to the spray solution was 4.8×10^{-4} M.

Fig. 6 shows the size distribution of the powders prepared at a pressure of 160 Torr from the spray solutions with and without PEG. In the SEM photograph shown in Fig. 2, the powders obtained from the aqueous spray solution had a broad size distribution. Low concentrations of PEG added to the spray solutions improved the size distributions of the powders. On the other hand, the geometric standard deviations of the powders increased with further increase of the concentrations of PEG added to the spray solutions. The geometric standard deviations of the powders as shown in Fig. 2(a), (b) and (c) were 0.3, 0.2 and 0.9. The change of the size distribution of droplets according to the concentrations of PEG added to the spray solution affected the size distribution of the powders. A low surface tension and viscosity of spray solutions with low concentrations of PEG decreased the size distributions of the droplets generated. On the other hand, a high viscosity of spray solutions with a high concentration of PEG increased the size distributions of the droplets.

The effects of reactor pressure on the mean sizes and morphologies of the powders were shown in Figs. 7 and 8. The reactor pressures were controlled from 60 to 400 Torr by changing the capacities of the vacuum pump. The mean sizes and size distributions of the powders were strongly affected by the reactor pressures. Fig. 7 shows the SEM photographs of the powders prepared from the aqueous spray solution at various pressures. The powders prepared from the aqueous spray solution at low pressure of 60 Torr had filled structure and fine size. On the other hand, the powders prepared at pressures of 240 and 400 Torr had hollow structures, large sizes and broad size distributions. Fig. 8 shows the SEM photographs of the powders prepared from the spray solution with PEG at various pressures. The concentration of PEG added to the spray solution was 4.8×10^{-4} M. The mean

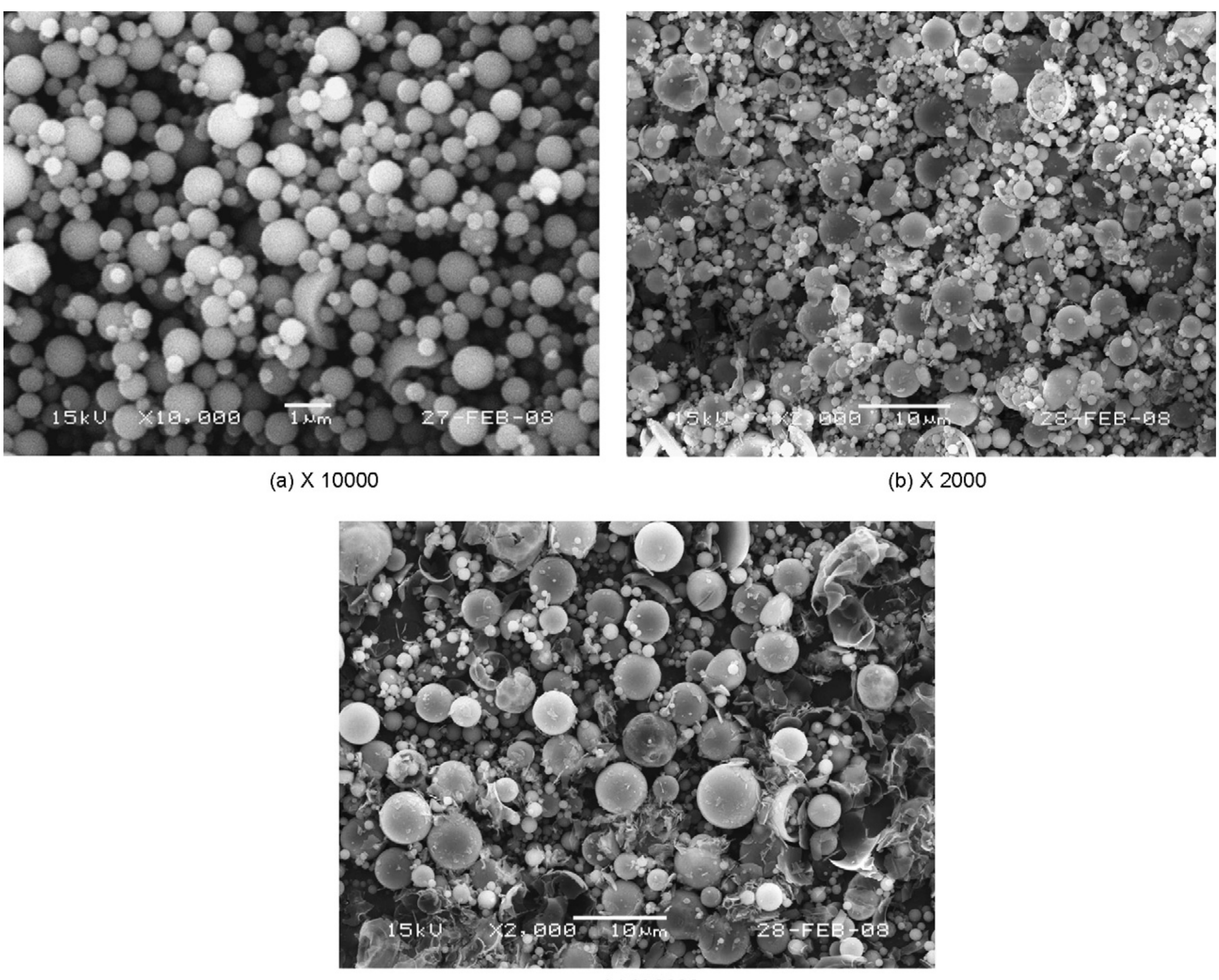

Fig. 7. SEM photographs of alumina powders prepared by FEAG process without organic additive from different reactor pressure (0.2 M Al nitrate, no additive, 900 °C): (a) 60 Torr, (b) 240 Torr, and (c) 400 Torr.

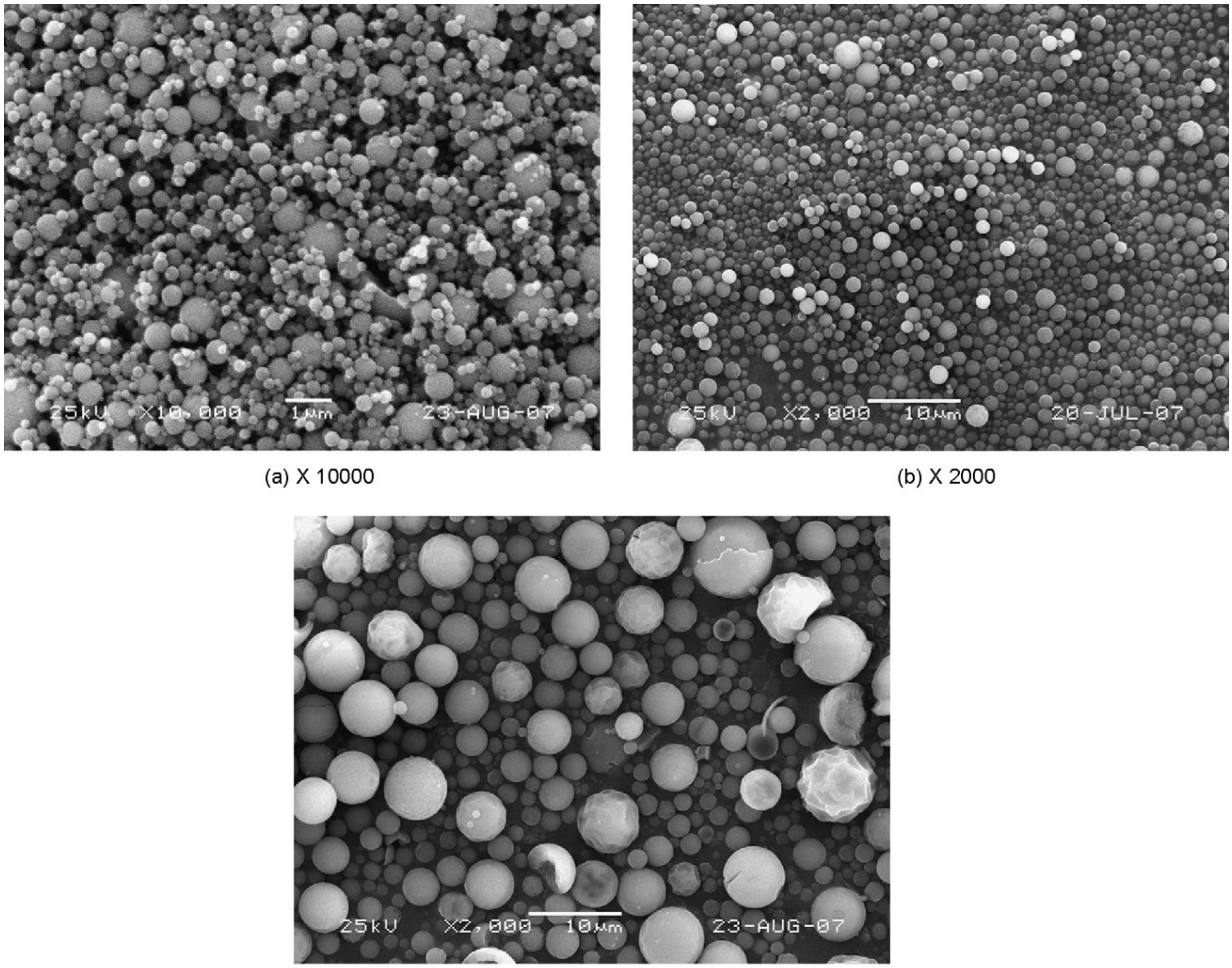

Fig. 8. SEM photographs of alumina powders prepared by FEAG process with organic additive from different reactor pressure (0.2 M Al nitrate, 4.8×10^{-4} M PEG, 900 °C): (a) 60 Torr, (b) 240 Torr, and (c) 400 Torr.

sizes of the powders were increased from 0.3 to 4.3 μm when the reactor pressure was changed from 60 to 400 Torr. The powders had a spherical shape and a dense structure irrespective of the concentrations of PEG added to the spray solutions. Therefore,

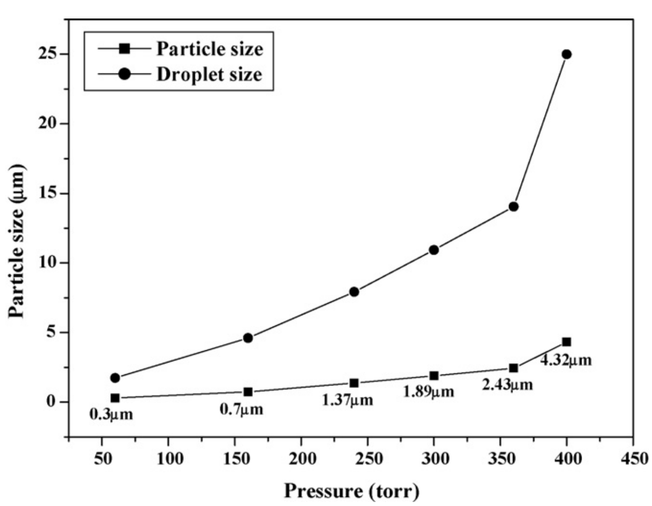

Fig. 9. Powder size and droplet size as a function of changing reactor pressure.

the change of the mean size of the powders according to the reactor pressures was caused by the difference of the mean size of droplets generated by the FEAG process. The mean sizes of powders measured from the SEM photographs are shown in Fig. 9. The mean sizes of the droplets calculated from Eq. (1) using the mean sizes of powders are also given in Fig. 9. The mean sizes of the droplets generated by the FEAG process changed from 1.7 to 25 μm when the reactor pressures were changed from 60 to 400 Torr. The powders prepared at pressures between 160 and 360 Torr had a narrow size distribution. On the other hand, the powders prepared at low and high pressures had broad size distributions because of instability in the FEAG process.

4. Conclusions

The effects of the surface tension and viscosity of the spray solutions on the characteristics of droplets generated by the FEAG process were investigated. The mean size of droplets decreased with the decreasing surface tension of the spray solution through the addition of a low concentration of PEG. On the other hand, the mean size of droplets increased with an increase of the viscosity of the spray solutions through the addition of a high concentration of PEG. The mean size of droplets was also strongly affected by the reactor pressure. Therefore, the mean size of droplets could be controlled from 1.7 to 25 μm by changing the concentration of PEG added to the spray solution and the reactor pressure.

References

1. Pike, R. D., Cui, H., Kershaw, R., Dwight, K., Wold, A., Blanton, T. N. *et al.*, Preparation of zinc sulfide thin films by ultrasonic spray pyrolysis from bis(diethyldithiocarbamato) zinc(II). *Thin Solid Films*, 1993, **224**, 221–226.
2. Lee, C. H. and Huang, C. S., Spray pyrolysis deposition for indium oxide doped with different impurities. *Mater. Sci. Eng. B*, 1994, **22**, 233–240.
3. Kodas, T. T., Sood, A. and Pratsinis, S. E., Submicron alumina powder production by a turbulent flow aerosol process. *Powder Technol.*, 1987, **50**, 47–53.
4. Kang, Y. C. and Park, S. B., A high-volume spray aerosol generator producing small droplets for low pressure applications. *J. Aerosol. Sci.*, 1995, **26**, 1131–1138.
5. Kang, Y. C., Park, S. B. and Kang, Y. W., Preparation of high surface area nanophase particles by low pressure spray pyrolysis. *NanoStructured Mater.*, 1995, **5**, 777–791.
6. Kang, Y. C., Chung, Y. S. and Park, S. B., Preparation of YAG:europium red phosphors by spray pyrolysis using a filter-expansion aerosol generator. *J. Am. Ceram. Soc.*, 1999, **82**, 2056–2060.
7. Kang, Y. C. and Park, S. B., Zn_2SiO_4:Mn phosphor particles prepared by spray pyrolysis using a filter expansion aerosol generator. *Mater. Res. Bull.*, 2000, **35**, 1143–1151.
8. Lenggoro, I. W., Itoh, Y., Iida, N. and Okuyama, K., Control of size and morphology in NiO particles prepared by a low-pressure spray pyrolysis. *Mater. Res. Bull.*, 2003, **38**, 1819–1827.
9. Wang, W. N., Itoh, Y., Lenggoro, W. and Okuyama, K., Nickel and nickel oxide nanoparticles prepared from nickel nitrate hexahydrate by a low pressure spray pyrolysis. *Mater. Sci. Eng. B*, 2004, **111**, 69–76.
10. Zhang, S. C., Messing, G. L. and Huebner, W., $YBa_2Cu_3O_{7-x}$ superconductor powder synthesis by spray pyrolysis of organic acid solutions. *J. Aerosol. Sci.*, 1991, **22**, 585–599.
11. Meesters, G. M. H., Vercoulen, P. H. W., Marijnissen, J. C. M. and Scarlett, B., Generation of micron-sized droplets from the Taylor cone. *J. Aerosol. Sci.*, 1992, **23**, 37–49.
12. Roh, H. S., Kang, Y. C., Park, H. D. and Park, S. B., Y_2O_3:Eu phosphor particles prepared by spray pyrolysis from a solution containing citric acid and polyethylene glycol. *Appl. Phys. A*, 2002, **75**, 1–5.
13. Bird, R. B., Amstrong, R. C. and Hassager, O., Dynamics of polymeric liquid. *Fluid Mechanics*. Wiley-Interscience, New York, 1987, p. 1.