Nanosized particle synthesis by Flash Boiling Atomization

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Abstract

An innovative nanosized metal particle synthesis method by flash boiling atomization is proposed. Methane-oxygen premixed flame is utilized as the heat source and the precursor water solution is sprayed into the low-pressure field. Then, droplets are secondary-atomized by flash boiling phe-nomenon. The zinc acetate water solution is used as the precursor to synthesize ZnO nanosized metal particles. From the view point of industrial aspects, the size controllability of nanosized metal particle, the inhibition of agglomeration and the inexpensive large production quantity are required for the particle synthesis method. The synthesis method, which is presented in this paper, is expected to achieve the above-mentioned characteristics. In this paper, firstly, the flashing spray is observed by using Mie scattering method. Secondly, ZnO nanosized metal particles are synthesized to investigate the effect of the flash boiling atomization on the synthesized particles. It was found that the droplets were well atomized and dispersed when the flash boiling phenomenon occurred. In addition, the higher the temperature of precursor solution became (above the saturated temperature), the smaller the synthesized particles were.

Introduction

A powder particle is one of the most basic materials used as ceramics, semiconductor, sintered materials, and other electrical devices. Especially, the fine particles of 100 nm or less in the size are called as nanoparticles. The nanoparticles have some special characteristics resulted from the quantum effect. Those characteristics are never seen in bulk material [1]. Therefore, nanoparticles are the bedrock of nanotechnology and very valuable. From the view point of industrial aspects, the nanosized particle synthesis method is required high quantities of mono-dispersed particles. Currently, the chemical vapor deposition (CVD) method is one of the most commonly used nanosized particle synthesis methods. The CVD method has several advantages in the controllability of particle size and particle purity. The CVD method, however, has negative aspect in the particle productivity because it is difficult to supply precursor vapor continuously. Other particle synthesis method, such as spray pyrolysis (SP) method, can synthesize particles continuously. However, in general, fine particles less than submicron in the size cannot be synthesized by SP method [2]. In this paper, we propose the nanosized particle synthesis method by flash boiling atomization. Figure 1 shows the schematic diagram of this method. Methane-oxygen premixed flame is utilized as heat source and the precursor water solution is sprayed in the low-pressure combustion field. Then, the precursor spray is rapidly evaporated by the flash boiling atomization [3] and pyrolized, and nanosized particle is synthesized. It is expected that the nanosized particle synthesis method by the flash boiling atomization can achieve the above-mentioned characteristics (nanosized particle synthesis with high productivity).

In this paper, firstly, the flashing spray is observed by using the Mie scattering method. Secondly, ZnO nanoparticles are synthesized to investigate the effect of the flash boiling atomization on the characteristics of the synthesized particles.

Experimental setup

Figure 2 shows the schematic diagram of experimental apparatus. The experimental apparatus consists of the gas supply system, the precursor solution supply system, the burner, the combustion chamber, and the particle trapping system.

Methane, which is the main component of city gas, is utilized as the fuel and oxygen as the oxidizer considering the ignition performance and flame stability at low-pressure field. Methane and oxygen are supplied by mass flow

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controllers and mixed in the mixing chamber. Then, the premixed gas is supplied to the burner. In this method, the oxidation atmosphere in case of lean combustion and the reduction atmosphere in case of rich combustion can be realized by controlling the equivalence ratio of the premixed gas. Therefore, it is expected that both oxidized particle and pure metal particle can be synthesized by this method.

Precursor water solution is supplied from the pressure cylinder. The flow rate of the precursor water solution is controlled by the mass flow controller and supplied to the spray nozzle set at the center of the burner. In this experiment, the spray nozzle with return system (EVERLOY: BN 2.6-68) is utilized. This nozzle can make a fine spray in wide range of flow rate. In order to make the flash boiling atomization, it needs to control temperature of the precursor water solution higher than the saturated temperature [3]. In this experiment, the temperature of precursor water solution was controlled by the hose heater between the mass flow controller and the spray nozzle.

The vitiated coflow burner (VCB) [4] which is thick metal plate punched 1.5 mm holes at even intervals was utilized. The schematic diagram of the VCB and the direct photograph of the premixed flame are shown in Fig. 3 and Fig. 4, respectively. The VCB forms many small premixed flames, so this burner can form the uniform temperature field for the radial direction (See Fig. 4). The spray nozzle is set at the center of the burner and a hollow-corn spray is formed above the VCB as shown Fig. 3.

The combustion chamber is made of stainless pipe and there are three quarts windows on the side wall. Those windows are set for observing the flame and the spray. The VCB is inserted from the bottom of the combustion chamber. Ignition of the premixed gas is conducted by the spark plug. The height of the combustion chamber is 622.5 mm, and six thermocouples are set at the center and side wall of the combustion chamber, of which height are 202.5, 377.5, and 552.5 mm above the burner.

Exhausted gas with the synthesized particles was vacuumed from the exhaust port at the top of the combustion chamber and the synthesized particles were trapped on the sintered metal filter (KOEI: JMCW-01-002-V). The steam in the exhausted gas was trapped at the cold-trap with liquid nitrogen and the exhausted gas was evacuated to atmosphere by the vacuum pump (ULVAC: VD401). Pressure in the combustion chamber was monitored by the digital manometer and controlled by inducting the ambient air to the combustion chamber. Synthesized particles were observed by SEM.

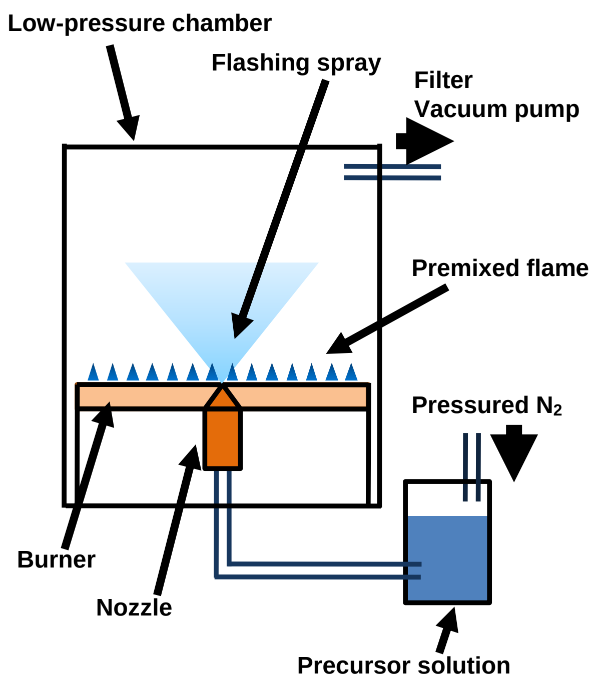

Figure 1. Schematic diagram of particle synthesis by the flash boiling atomization

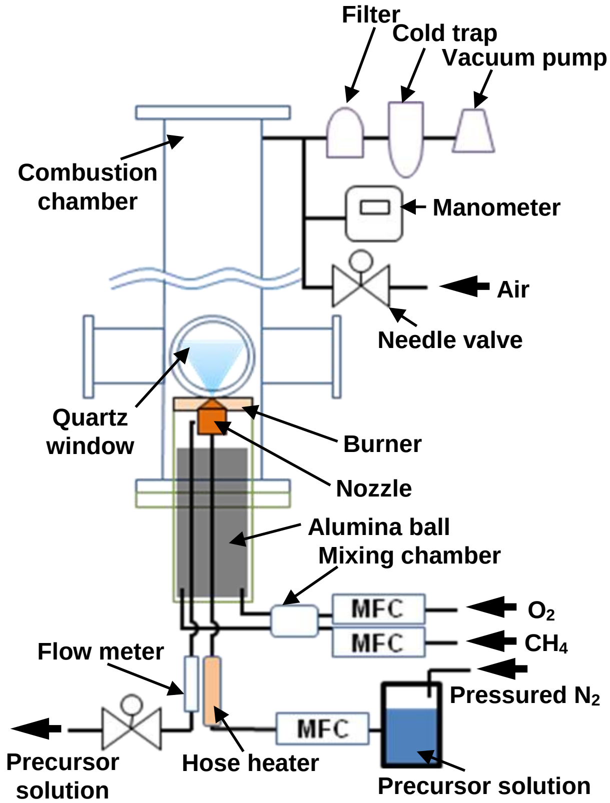

Figure 2. Schematic diagram of the experimental apparatus

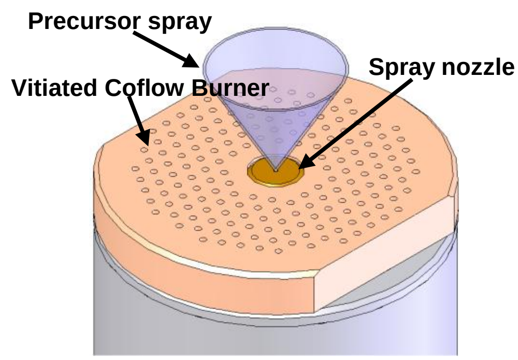

Figure 3. Schematic diagram of the vitiated coflow burner

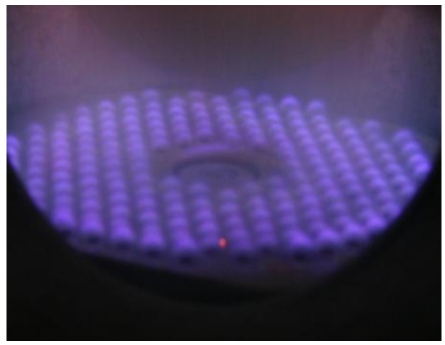

Figure 4. Photograph of methane oxygen premixed flame

Experimental conditions

The objective material of this study is ZnO. ZnO is expected to be the commutation of Indium Tin Oxide (ITO) which is used as limpid emitter of liquid crystal panel display or light-emitting device [5]. There is a possibility to synthesize submicron particles of ZnO by the spray pyrolysis method [6]. The zinc acetate water solution was used as a precursor material, considering the poisonous property for human. In order to avoid the deposit on the quarts windows, pure water was used as the commutation of the zinc acetate water solution in the experiment of spray visualization by the Mie scattering method.

The flash boiling atomization phenomenon is affected by the saturated vapor pressure. In this experiment, zinc acetate water solution is dilution, and there is little difference of saturated vapor pressure between pure water and the zinc acetate water solution employed in the present study. The comparison of the saturated vapor pressure between pure water and the zinc acetate water solution (concentration is 13.9 wt%) is shown in Fig. 5. The saturated vapor pressure of zinc acetate water solution was calculated by Raoult's law [7].

Spray visualization by Mie scattering method

To investigate the initial stage of the flash boiling atomization phenomenon, The Mie scattering method is conducted for the visualization of spray. Table 1 shows the experimental conditions for the spray visualization. Pressure in the combustion chamber, flow rate and equivalence ratio of the premixed gas and flow rate of the water is 18 kPa, 12 L/min, 0.8 and 2200 g/h respectively [8]. In the employed pressure range, the saturated temperature is about 46 ~ 58 °C (See Fig. 5). Therefore, the temperature of water is determined to (a) 39 °C (subcool condition), (b) 50 °C (cross point), (c) 70 °C (superheated condition). In each condition, the spray visualization by the Mie scattering method was conducted.

ZnO particle synthesis

ZnO nanoparticles are synthesized to investigate the effect of flash boiling atomization on the synthesized particles. Table 2 shows the experimental conditions for the ZnO particle synthesis. The pressure in the combustion chamber, the flow rate and the equivalence ratio of the premixed gas was determined referring to our previous report [8]. The flow rate of the zinc acetate solution is 900 g/h, the temperature of the zinc acetate water solution is 30 ~ 70 °C.

Table 1. Experimental condition for spray visualization

Case number	(a)	(b)	(c)
Pressure kPa	18		
Premixed gas flow rate L/min	12		
Equivalent ratio	0.8		
Flow rate of water g/h	2200		
Temperature of water °C	39	50	70

Table 2. Experimental conditions for ZnO particle synthesis

Case number	1	2	3
Pressure kPa	10		
Premixed gas flow rate L/min	12		
Equivalent ratio	0.8		
Concentration of zinc acetate wt%	13.9		
Flow rate of zinc acetate solution g/h	900		
Temperature of zinc acetate solution °C	30	50	70

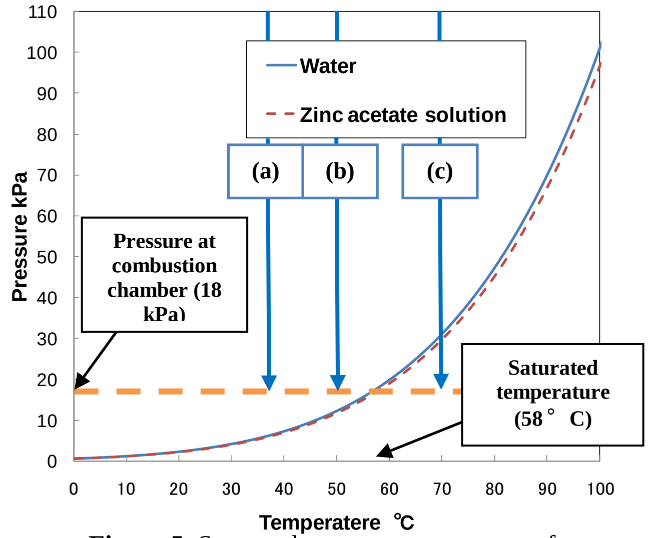

Figure 5. Saturated vapor pressure curve of pure water and zinc acetate solution

Result of spray visualization

Figure 6 shows the visualized spray image in the condition of that pressure in the combustion chamber is 18 kPa and flow rate of water is 2200 g/h.

The ambient pressure decreases drastically and instantaneously from 0.6 MPa to 18 kPa by spraying from the pressure atomizer in the combustion field. If the temperature of the sprayed water is higher than the saturated temperature (e.g. 58 °C at the 18 kPa), flash boiling and phase transition will occur at the inside of the water droplets. It can be clearly understood from Fig. 6 that, in condition (a) and (b) (temperature of sprayed water is subcooled condition), a normal hollow-corn spray is observed. On the other hand, in condition (c) (temperature of the sprayed water is superheated condition), the flash boiling atomization occurs and the spray well disperses. Especially, spray droplets are observed inside the hollow-corn spray. And even in other conditions in which the flow rate of water varies, the similar trend that spray droplets are well atomized when the flash boiling atomization occurs is observed. In addition, the higher the temperature of water becomes, the more strongly flash boiling atomization occurs.

With the above-mentioned reason, by applying flash boiling atomization, it can be possible to utilize the spray nozzle with high flow rate by accelerating evaporation of the precursor solution. As a result, it can be possible to synthesize nanosized particles with high productivity. In particular, in this experiment we use the spray nozzle of which the supply rate is about 500 ~ 1000 mL/h, by contrast with the nebulizer commonly used in spray pyrolysis of which the spray rate is about 10 ~100 mL/h.

Result of ZnO particle synthesis

The SEM images of the synthesized ZnO particles under conditions 1, 2 and 3 are shown in Figs. 7 (a), (b), (c), respectively. In cases 2 and 3 in which temperature of the zinc acetate solution is higher than the saturated temperature, nanosized ZnO particles were synthesized successfully (See Fig. 7). Especially, uniformly-sized spherical nanoparticles about 20 nm in diameter were synthesized in case 3. It can be considered that the spray droplets are well atomized and rapidly vaporized by the flash boiling atomization and the precursor vapor uniformly formed. In addition, particles in the rod shape of about 100 nm length are partially synthesized in case 2 (See the circle in Fig. 7 (b)). Therefore, it is found that the smaller particles can be synthesized by utilizing the flash boiling atomization.

In contrast, the particle synthesis ends in failure in case 1. Effects of the heat supply and the flow rate of precursor solution on ZnO particle synthesis are investigated [9]. In this experiment, it is estimated that the particle synthesis is in failure because of the insufficiency of the heat supply compared to the precursor supply. It indicates that the precursor supply can be increased by applying flash boiling atomization.

As the future work, we are going to investigate the relationship between characteristics of the flashing spray and the synthesized particle by conducting the quantitative measurement of the flashing spray and the synthesized particle.

Conclusion

The innovative nanosized particle synthesis method by flash boiling atomization was proposed in this paper. In addition, in order to investigate the availability of this method, the visualization of flashing spray and synthesis of ZnO particle are conducted. The main findings were as follows;

1. Spray droplets were well atomized and dispersed when flash boiling occurred.
2. By applying the flash boiling atomization, the synthesis of nanosized particle with high productivity was achieved.
3. The higher the temperature of precursor solution became above the saturated temperature, the smaller the synthesized particles were.

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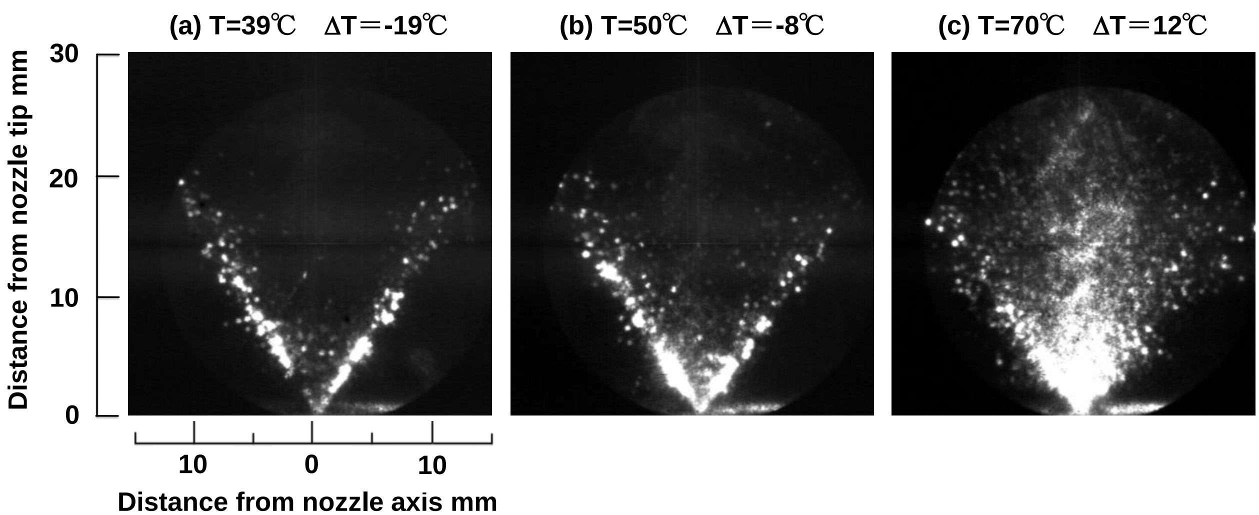
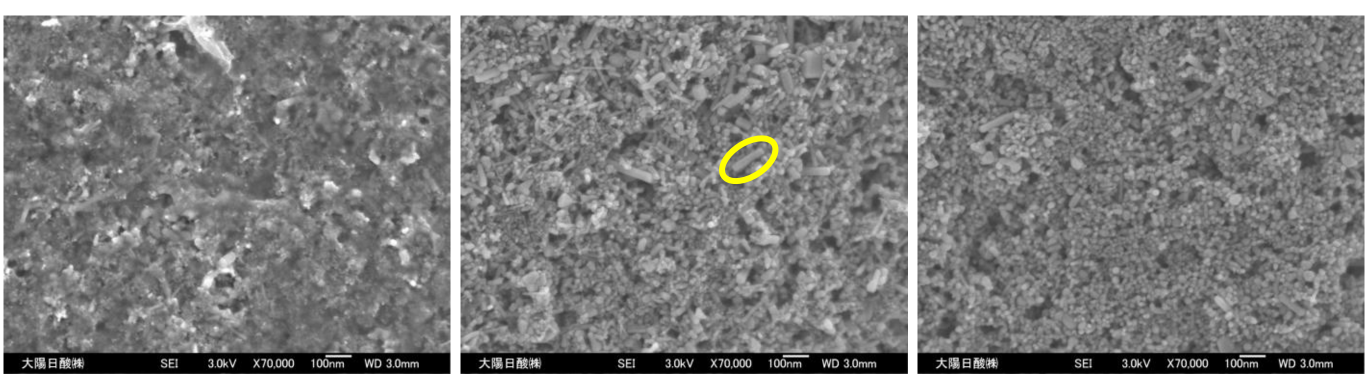


Figure 6. Visualization of flashing spray
T shows the temperature of water
ΔT shows the degree of superheat



(a) case 1 (b) case 2 (c) case 3

Figure 7. Effect of the flash boiling atomization on the ZnO particles