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기상반응에 의한 철 초미립자 제조시 입자크기분포 제어

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Control of Particle Size Distribution of Ultrafine Iron Particles in the Gas Phase Reaction

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INTRODUCTION

Ultrafine metal particles of less than 100 nanometer in particle size find many applications as new materials for magnetic tape, catalyst, sensors and sintering additives, etc[1]. Ultrafine iron particle is used for high density recording media and used in sintering additives, etc.

Synthesis of ultrafine metal particles by gas phase reaction is reported by many researchers[2,3,4,5]. Previous researchers have investigated the effective variables on the production of ultrafine particles such as reaction temperature, partial pressure of feed, residence time of feed in reaction zone. However, previous results did not focused on the control of particle size distribution of produced ultrafine particles. Lee[6] suggested theoretical results that initial size distribution of aerosols had a rather pronounced effect on the coagulation rate and then played the very important role to the final size distribution of aerosols. However, there was no experimental result on the effect of initial size distribution.

The purpose of this study is to investigate the effects of the initial distribution of reactant to the final particle size and distribution of produced ultrafine particles experimentally. However, it is impossible to detect the initial distribution of reactant directly during the vapor phase synthesis of ultrafine particles. Therefore, we adopted indirect method which could expect the initial state of reactant from particles produced by reaction. For the indirect method, two experimental variables were chosen as follows; variation of evaporating temperature in the same evaporation rate of ferrous chloride, and temperature gradient of reactants between preheating zone and reaction zone. The effects on the such variables to the particle size distribution were investigated experimentally.

EXPERIMENTAL

A schematic drawing of experimental apparatus is shown in Fig. 1 consisting of gas purification, reaction, particles collection and off-gas treatment part, and data acquisition and control part by computer.

A multi-stage aerosol reactor was made of quartz tube and was consisted of evaporation for $FeCl_2$, preheating of $FeCl_2$ vapor and H_2 gas, and reaction part where reactants meet. The total length of reactor was 155cm, the diameter of reaction part was 3.0cm and length of reaction part was 75cm. $FeCl_2$ was loaded in quartz boat connected with load cell for the measuring of weight change. Preheating part for reactants was composed of double pipe and the length of preheating part 40cm. Argon gas and $FeCl_2$ vapor flow through the inner tube, and H_2 gas flows through the outer tube. The nozzle for the mixing of reactants was installed before the reaction part. The tube furnace is composed of four pieces of heater which controlled temperature separately by computer. The first one was for evaporation, the second one was for preheating, and the third and the fourth ones were for reaction to control the temperature distribution of axial direction. Produced ultrafine particles was collected by using teflon membrane filter which has a 20 micron meter in average pore size.

For the measurement of particle shape, size and distribution, transmission electron microscope was used. The particle size and distribution were determined by counting the more than 500 particles from TEM pictures. The geometric standard deviation which represents the particle size distribution of the particles was obtained by log-probability plot. The x-ray diffraction patterns were obtained by a X-ray diffractometer. Ion meter was used for the measuring of reactivity.

RESULTS AND DISCUSSION

Effect of evaporating condition in the constant evaporation rate of $FeCl_2$

Ferrous chlorides vapor in the evaporating zone could have a distribution which is composed of molecule clusters and may have different size distribution of molecule clusters when it meets with carrier gas in the different situation of the evaporation[7]. Such a $FeCl_2$ vapor react with hydrogen in the reaction zone through preheating zone, and then Fe clusters having some size distribution could be produced. The big Fe clusters among the iron clusters could have a fast growth rate to nuclei than small clusters. If the Fe vapor has a uniform size distribution of clusters, all the clusters will have same growth rate and then uniform particle in size could be produced.

We investigated considered two possible ways to control the initial size distribution of $FeCl_2$ clusters with variation of evaporation condition of reactant as follows;

(A) Change of the evaporation temperature at constant surface area.

(B) Change of the surface area at constant evaporation temperature.

The change on the evaporation rate of $FeCl_2$ due to the variation of evaporation state are maintained same rate in the both cases. In the case of (A), flux of $FeCl_2$ vapor increase as the evaporation temperature increase. Then, the local density of $FeCl_2$ vapor increase and probability of collision between $FeCl_2$ molecules. Therefore, clusters which has different in size will dominantly form. However, in the case of (B), the local density could not be so high than local density in the case of (A) because the flux of $FeCl_2$ vapor is low in the large surface area. Then, clusters in the case of (B) may be more uniform in distribution than cluster in the case of (A). The experiments was made at the condition of same preheating and reaction zone temperature, and constant gas flowrate. Iron particles were obtained with different evaporating conditions at the same evaporation rate of $FeCl_2$. There were differences in particle size and size distribution of between two different evaporating conditions. Particles obtained at the condition of (A) were more small and uniform in size than particles of condition (B)(Fig.2).

Effect of temperature gradient of reactants between preheating zone and reaction zone

Temperature gradient of reactants between preheating zone and reaction zone is very important from the viewpoint of nucleation in the gas phase reaction because nucleation is very dependent on temperature. Such temperature gradient could also effect the particle size and size distribution during the gas phase reaction. Therefore, we considered two cases of temperature gradient from the standpoint of nucleation at the condition of constant evaporation rate of $FeCl_2$, and gas flow rate as follows;

(C) : reactants are injected each other at the temperature of 700℃ to the reaction zone at the temperature of 900℃.

(D) : reactants are injected each other at the temperature of 900℃ to the reaction zone at the temperature of 900℃.

In the case of (C), some of these reactants could react from low temperature, so some particles could be produced at low temperature(700℃). Such particles will play a role as seeds when the nucleation occurred at the zone of the determined reaction temperature(900℃) and also grow until temperature of reactants reaches to the determined reaction temperature(900℃). Then there exist large particles from nucleation in the low temperature and small particles from nucleation in the high reaction temperature, and it is difficult to obtain uniform particles under such a condition. However, in the case of (D), reactants meets together at the determined temperature(900℃), so the more uniform particles could be produced at the determined reaction temperature than the particles in the case of (C).

Fig. 3 shows the effects of temperature gradient between preheating and reaction zone on the particle size and distribution of ultrafine iron particles. As the temperature gradient decreased, average particle size of iron particles was decreased and particle size distribution became more uniform.

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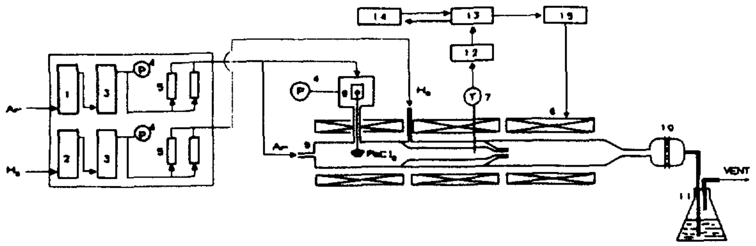

Fig.1. Schematic diagram of experimental apparatus.

1. Copper powder column
2. O2 removing purifier
3. Gas purifier
4. Pressure indicator
5. Flowmeter
6. Load cell
7. Thermocouple
8. Tube furnace
9. U.F.P. reactor
10. Powder collector
11. HCl absorber
12. Amplifier
13. A/D D/A converter
14. Computer
15. SCR

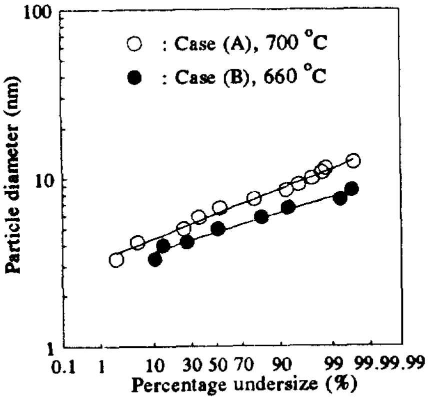

Fig.2. Log-probability plots of the iron particles with different evaporating conditions at the same evaporation rate(0.008 g/min).

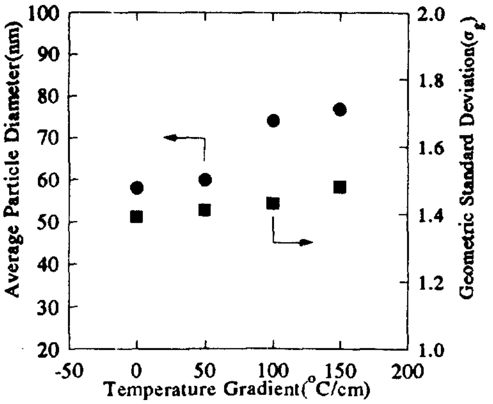

Fig. 3. Effect of temperature gradient on the particle size and size distribution(Reaction temp.: 900°C, $FeCl_2$ Feedrate : 0.02 g/min,Gas flowrate : 10 l/min).