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Preparation of Ultrafine Oxide Powders by Inductively Coupled Plasma Generated with Modified Conventional Induction Heater*

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Synopsis

Ultrafine oxide powders (MgO and ZrO_2, 0.01 μm order of size) were prepared by spraying nitrate solutions into an argon inductively coupled plasma of ultra-high temperature (ICP). A conventional induction heater (5 kw, 400 kHz and thyratron-controlled) was modified for generating the argon ICP flame. The basic modification consisted in increasing its power and frequency (15 kw, 4-16 MHz and thyristor-controlled). In order to quench the formed powders rapidly, a water-cooled powder collector was used. The particle shape of the magnesium oxide was not cubic but roundish, and the main phase of the zirconium oxide was metastable tetragonal-ZrO_2. These suggest that the powders formed by ICP should be quenched so rapidly that they could not grow large or could not convert to high temperature phases. The particle size distribution of the magnesium oxide followed the Gaussian type of formula proposed by Aboav (range 0.016-0.044 μm, modal diameter 0.028 μm).

I. Introduction

The inductively coupled plasma (ICP) generated under atmospheric pressure with a radio-frequency oscillator is an appropriate heat source for promoting chemical reactions at ultra-high temperatures. ICP is an electrodeless plasma, therefore even corrosive reactions such as oxidation, etching, etc. can be progressed in ICP. Moreover, the contamination by electrodes can be avoided. Since the first report of ICP by Reed[1], ICP has been extensively used for emission

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spectroanalysis, crystal growth, preparation of ultrafine powders, refinement of metals and so on. In ICP, the time of reactants being in an ultra-high temperature zone is longer than in an arc or in a plasma jet[2], which is favorable for the completion of reactions. In addition, products are rapidly quenched from a temperature of plasma above 5000 K to 200-300 °C, which fits to the preparation of ultrafine powders.

Recently ultrafine powders have been recognized as important starting materials for the production of fine ceramics. When ICP is used as a heat source for the preparation of ultrafine powders, gaseous or solid reactants, hitherto, have been fed to ICP. However, feeding a solution to ICP by a spray method can also be applied in obtaining well distributed ultrafine powders and particularly is suitable for the preparation of solid solution of ultrafine oxide powders, because the concentrations of each component are easily adjusted when the solution is prepared. In the present paper, the modification of a conventional induction heater for generating an argon ICP flame and the experimental procedure for the preparation of magnesium oxide and zirconium oxide have been described in detail. As the properties of ultrafine powders of these oxides are sensitive to the precipitation conditions[3,4], they are appropriate for diagnostic indicators for the improvement of the experimental techniques.

II. Experimental procedure

1. Modification of oscillator

Table 1 summarizes the points of modification. The conventional induction heater was manufactured in 1957. An air cooled vacuum tube was used for amplifying oscillation (OSC-VT). The tank circuit was

Table 1. Modification of conventional oscillator.

	conventional	modified
max. output	5 kw	15 kw
frequency	400 kHz	4-6 MHz and 400 kHz
output control	thyratron	thyristor
output AVR	no	yes
OSC VT fil. AVR	no	yes
tank circuit	plate coupling	plate coupling
temp. controller	no	yes

plate coupling type. The output was controlled with thyratrons, mercury VT rectifiers and an inductive phase shifter. The maximum power and the frequency were 5 kw and 400 kHz, respectively. Figure 1 illustrates the block diagram of the oscillator modified. The basic modification consisted in not only increasing its power and frequency (15 kw, 4-16 MHz) but also exchanging the thyratron-rectifying circuit with a thyristor-controlled unit, while the tank circuit for 400 kHz oscillation was left for the conventional induction heating with minor changes. The mercury VT rectifiers and the thyratrons were exchanged with silicon diode rectifiers and thyristors, respectively. The former was inserted in the secondary of a step-up transformer and the latter was in the primary as open-delta control. The thyristors were protected from the damage due to surge current with a circuit protector. With this modification, the output voltage could be regulated automatically (AVR). Additionally, an automatic temperature controller could be connected to the oscillator for the conventional induction heating. These were easily carried out by feeding back the output voltage or the voltage of temperature sensors to the gate circuit of the thyristors. The OSC-VT was exchanged with a water-cooled VT. In order to minimize the consumption of water, cooling water was supplied with the control system regulating the level, pressure and temperature of the water. The OSC-VT was protected from overload by the current limiters put in plate and grid current circuits. The filament voltage was maintained constant by another thyristor unit. The initial rush current in the filament was restricted by a current-limiting circuit. The tank circuit for generating ICP was newly constructed. As the result of taking into account the ease of adjusting frequency and of matching, a plate coupling type of tank circuit was adopted. The voltage power supply for the 400 kHz tank circuit was commonly used for the 4-16 MHz one. In order to avoid the discharge and the interference between parts due to high frequency and high power, much attention was paid to the distance between the parts and their location.

2. Preparation of ultrafine powders of MgO and ZrO_2

Figure 2 shows the schematic diagram for the spray method. In the present study, one component oxide systems such as MgO and ZrO_2 were chosen for the technical improvement of this method. The solutions were prepared by dissolving guaranteed grade $Mg(NO_3)_2 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ into distilled water (concentration 0.5-2M). The solutions were sprayed into a spray chamber with the coaxial type of nebulizer, which was the same as the one used in ICP emission

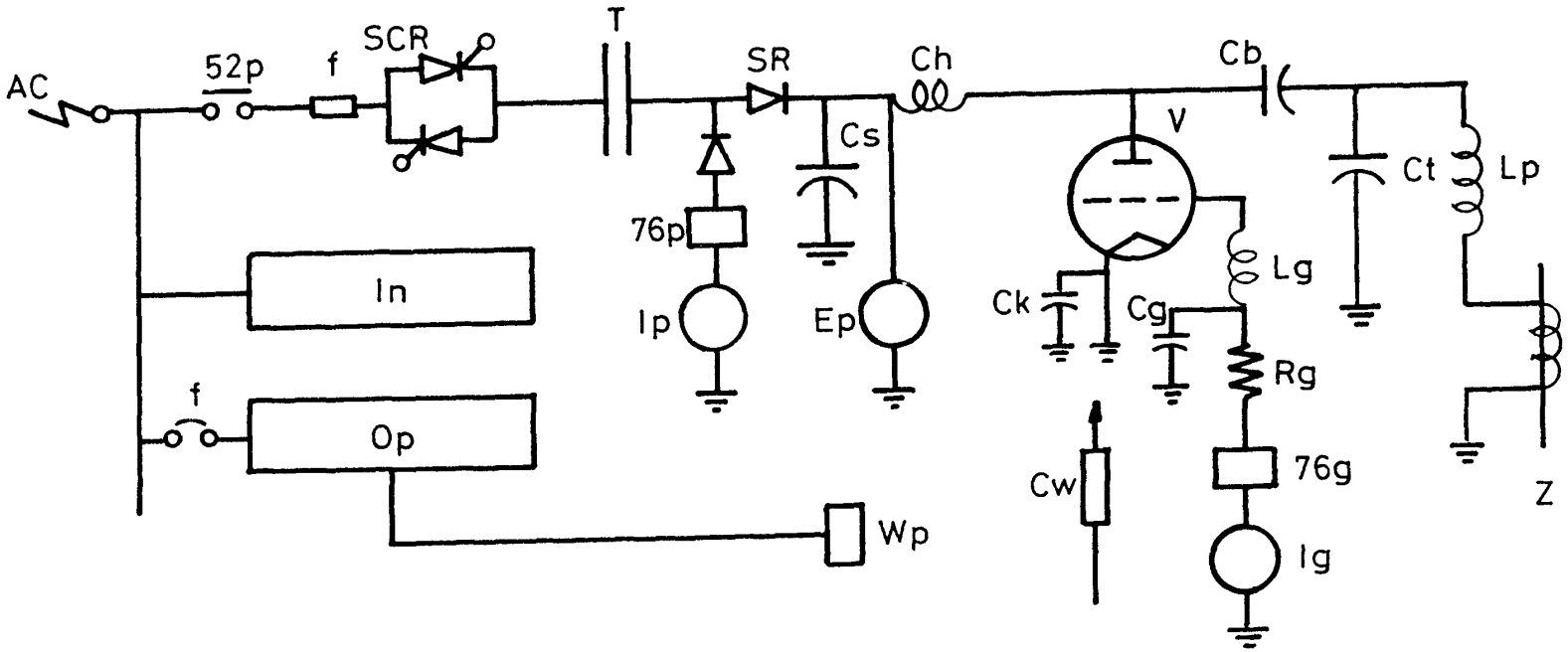

Fig. 1. Block diagram of modified oscillator

AC	AC source
SCR	thyristor
Wp	water pressure switch
76p	plate overcurrent relay
Ch	high-frequency choak
Ck	filament by-pass condenser
Cg	grid by-pass condenser
Ig	grid ammeter
Lp	plate coil
52p	magnetic switch
In	indicator
T	step-up transformer
Ip	plate ammeter
Ep	plate voltmeter
Cw	cooling water
Rg	grid leak
Cb	coupling condenser
z	ICP
f	circuit protector
Op	operation circuit
SR	silicon diode
Cs	smoothing condenser
V	vacuum tube
Lg	grid coil
76g	grid overcurrent relay
Ct	tank condenser

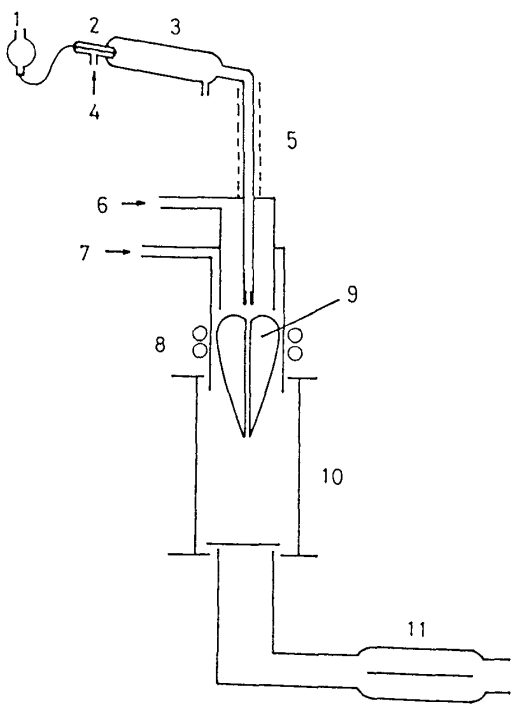

Fig. 2. Schematic diagram for the spray method with ICP, (1) reservoir, (2) nebulizer, (3) spray chamber, (4) carrier gas, (5) heated tube, (6) plasma gas, (7) cooling gas, (8) r. f. coil, (9) ICP, (10) collector, (11) electrostatic powder collector.

spectroanalysis[5]. The solutions were beforehand filtered (Millipore filter, 0.22 μm pore size) for keeping the nebulizer from being blocked. 1 l/min argon was flowed as a carrier gas. In the spray chamber (60 mm in diameter, 250 mm in length), large droplets were precipitated and only small droplets were introduced into the argon ICP flame after quick drying in a heated tube. The droplet sizes were measured by receiving the droplets on silicone oil spread on a glass slide. The feeding rates of the solutions to the argon ICP flame were estimated from the difference between the rates of inflow and drain of the solutions at the spray chamber.

A plasma torch was composed of a torch head, coaxial double quartz tubes and a nozzle. The argon ICP flame of 40 mm in diameter and 160 mm in length was generated with this torch. The quartz tubes and the nozzle were adjustable for symmetrizing the flame with respect to the coaxis[6]. In order to protect the outer quartz tube, 25 l/min argon cooling gas was introduced through the outer guide to the surface of the argon ICP flame from a tangential direction. A plasma gas was led through the inner guide to the ICP flame, and if necessary, 1 l/min nitrogen plasma gas could be introduced without extinguishing the flame.

The powders formed by ICP were precipitated in the following collectors (a) a quartz tube of 140 mm in inner diameter x 500 mm in length, (b) a quartz tube of 70 mm inner diameter x 500 mm in length, and (c) a water-cooled tube of the same size as (b). At the final stage of the system, an electrostatic powder collector was placed for the further collection of the powders.

The characterization of the prepared powders was carried out by transmission electron microscopy (Hitachi HU-11) and powder X-ray diffraction (Rigaku Denki, a diffractometer with the monochrometer having a curved graphite crystal). The particle sizes of the

prepared powders were determined by measuring the diameters equarlly dividing the area of the particle images on transmission electron micrographs. In this measurement, the direction of all the diameters was fixed to one direction --- the Martin's diameter[7].

III. Results and discussion

The actual feeding rates of the solutions to the argon ICP flame were 4-8 ml/hr. The droplet sizes ranged from 0.1 to 1 μm. It was reported that an iron particle smaller than 30 μm is considered to be evaporated completely while it passes through the argon ICP flame[8]. In view of this, the droplets in the present study seem to be small enough for the complete decomposition to their component atoms in the argon ICP flame. The generated argon ICP flame was the doughnut type in which the sprayed droplets passed through the low temperature channel along the coaxis of the flame[9]. When a large tipped nozzle was used, the argon ICP flame became a ellipsoid type and some droplets passed along the surface of the flame without being decomposed.

The collectors have a large effect on the properties of the powders prepared. Figure 3-A and 3-B show the transmission electron micrographs of the magnesium oxide precipitated in the collector (a) and (b), respectively. When the collector (a) was used, the

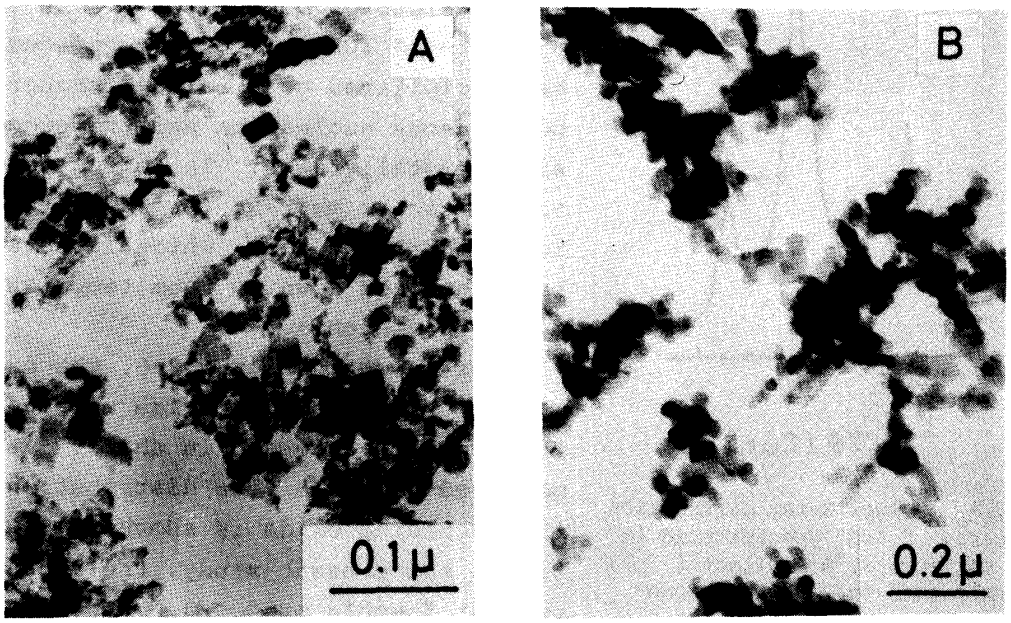

Fig. 3. Transmission electron micrographs of MgO precipitated in the collectors, A; collector (a), B; collector (b).

magnesium oxide powder contains cubic particles. These cubic particles are the same as those formed by firing metallic magnesium in the air[10]. On the other hand, when the collector (b) is used, only roundish particles of uniform size were formed. These suggest that in the collector of large diameter, some of the particles should touch the flame again and could grow into the cubic particles, while in the collector of small diameter the chance of touching seems to be much decreased.

Figure 4 illustrates the powder X-ray diffraction patterns of the zirconium oxides precipitated in the collectors (b) and (c). In both the collectors, the main phase of the zirconium oxide was metastable tetragonal-ZrO_2 (mt-ZrO_2), and the minor was monoclinic-ZrO_2 (m-ZrO_2). However, when the collector was water-cooled---collector (c), the amount of mt-ZrO_2 was strikingly increased. Consequently the collector (c) was the most suitable for the preparation of the ultrafine oxide powders having particles of uniform size, shape and phase. The result that mt-ZrO_2 is formed in spite of the ultra-high reaction temperature of ICP suggests the following reaction mechanism. After the complete decomposition of the droplets in ICP, the particles seem to be precipitated outside ICP through homogeneous nucleation and the successive crystal growth. In this step, the particles must be formed in the low temperature form, which appears to be maintained down to room temperature by rapid quenching.

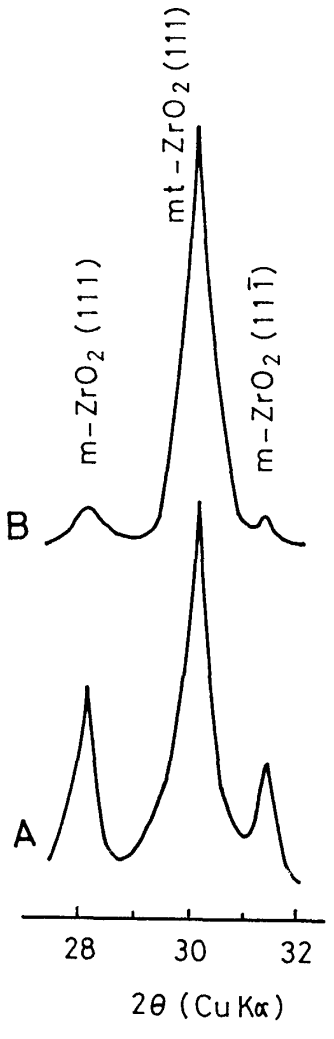

Fig. 4. Powder X-ray diffraction patterns of ZrO_2 precipitated in the collectors, A; collector (b), B; collector (c), m-ZrO_2; monoclinic-ZrO_2, mt-ZrO_2; metastable tetragonal-ZrO_2.

As shown in Figure 3-B, the particles of the magnesium oxide were uniform both in size and in shape. The measured particle size distribution of the magnesium oxide is shown in Figure 5. In the present study, the Gaussian type of formula proposed by Aboav (1)[11] has been applied to the particle size

distribution measured,

$$N = N_m \exp[-k\{(d/d_m)^{1/2} - 1\}^2] \qquad (1)$$

where N, d, N_m, d_m and k are number of particles, diameter, maximum N, d for N_m and constant, respectively.
The equation (1) is converted to the eq. (2),

$$\ln(N/N_m) = -k\{(d/d_m)^{1/2} - 1\}^2 \qquad (2)$$

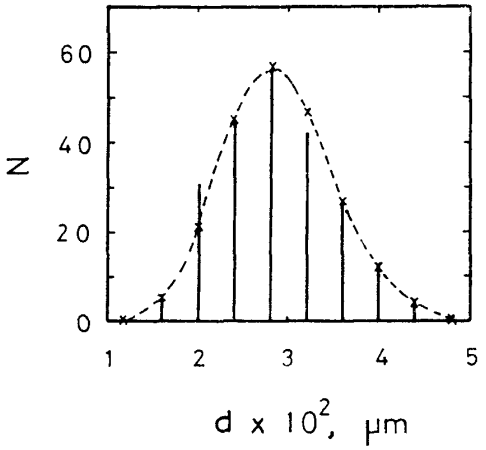

Fig. 5. Particle size distribution of MgO precipitated in the collector (b), N; number of particles, d; diameter. Broken line is the curve of best fit.

By the least-squares method applied to the plot of the right and the left side of the eq. (2), the relationship between N and d is obtained, which is illustrated with the broken line in Figure 5. Clearly, the particle size distribution of the magnesium oxide follows the Aboav's formula.

Summary

Ultrafine oxide powders (MgO and ZrO_2, 0.01 μm order of size) were prepared from nitrate solutions by the spray method with ICP. For the complete decomposition of the nitrates, ICP should be doughnut type. When a collector of narrow diameter was used, the particles of the prepared oxide (MgO) were uniform both in size and in shape. Additionally, when the oxide having isomorphs (ZrO_2) was prepared by this method, its main phase was the low temperature phase, which amount could be increased when the collector was water-cooled.

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