Preparation of Ultra-fine Alumina Powders by D. C. Plasma Jet

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Abstract–Ultra-fine alumina was prepared by DC thermal plasma. The influence of reactor configuration, input power and cooling conditions was investigated on properties such as particle diameter and phase composition. The powders synthesized without reaction tube were observed to be of two forms. One was metastable nano-sized powder with an average diameter of 30 nm due to rapid quenching of the vapor phase. The other form was larger-sized powder with an average diameter of 200 nm, and it was considered to be due to quenching of small liquid droplets, which had not fully vaporized in short residence time. With a reacting tube, the powder collected at the reaction tube was dominated by α-phase Al_2O_3, whereas the powder collected at the quenching chamber was mainly composed of intermediate γ- and δ-Al_2O_3. Input power and injection position of oxygen did not significantly affect the powder characteristics. To increase the conversion, aluminum powder should be vaporized completely. Most of the powders synthesized appeared fluffy spherical white powders with particle diameter of below 150 nm.

Key words: Plasma Synthesis, Phase Transition, Ultra-fine Powder, Rapid Quenching, Reactor Configuration

INTRODUCTION

Ceramic materials having a structure with ultra-fine size were found to exhibit properties markedly different from the same materials with larger grain sizes. These properties include improved hardness, ductility, and intriguing optical and electronic properties [Siegel, 1990]. For example, enhanced mechanical properties such as super-plasticity have been demonstrated in alumina, the most widely used ceramic material, for crystalline grain size below 500 nm [Chen and Xue, 1990]. These ultra-fine powders can be prepared through rapid quenching of materials from the gas phase.

Thermal plasma process has been demonstrated as an excellent method in synthesis of ultra-fine ceramic powders [Pfender, 1999; Kong and Lau, 1990]. The most explored feature in the applications to carry out high-temperature reactions followed by fast quenching, resulted in the formation of finely dispersed powders [Cruz and Munz, 1997]. Also, the great advantage of this process is that metal can be used in stead of chloride or organometallic compounds, which simplifies the process and makes the plasma processing economic. However, steep temperature and concentration gradients surrounding the plasma flame make gas-to-condensed phase conversion non-uniform and the process difficult to control, especially when it involves a reaction [Etemadi, 1991; Ageorges et al., 1993]. Numerous investigations have successfully demonstrated the use of novel plasma processing techniques for the generation of value-added materials [Taylor and Manrique, 1996; Oh and Park, 1997]. In these

applications, the particle morphology, size distribution, and phase composition are to the key characteristics which must be controlled.

The present work was aimed at investigating the influence of quenching conditions, plasma power, feed rate of raw material and reactor configuration on the properties of synthesized alumina particles. The particle morphology and phase transitions after heat treatment were observed for each process condition. Also, we tried to demonstrate the feasibility of the process control for plasma synthesis of ultrafine alumina.

EXPERIMENTAL

The DC plasma apparatus for synthesis of ultrafine alumina powder was shown in Fig. 1. This apparatus consisted of plasma torch, powder feeder, reaction tube, quench vessel, and exhaust-
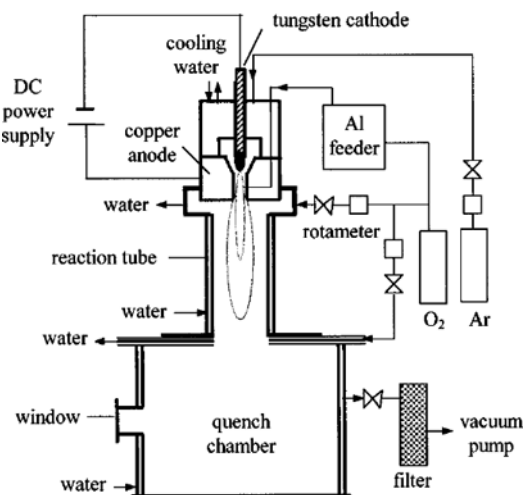

Fig. 1. Schematic diagram of DC thermal plasma apparatus.

Table 1. Experimental conditions

Plasma input power	8 kW-12 kW
Raw material	Purity: 99%, particle size: <20 μm
(Al powder)	(Kojundo Chemical Laboratory Co. Japan)
Flow rate of Ar gas	15 l/min
	Carrier gas for Al powder: 6-8 l/min
Flow rate of oxygen	Reaction tube: 2-5 l/min
	Quench chamber: 5-10 l/min
Operating time	5 minutes

ing part. Plasma was discharged between a tungsten cathode and copper anode using Ar gas at atmospheric pressure. The plasma torch typically ran with power from 8 kW to 12 kW. The reaction tube was made up of water-cooled stainless steel tube (length: 400 mm, inside diameter: 45 mm). Al powder was injected into the plasma flame through two holes in the anode nozzle by powder feeder (Metco 4 MP, Perkin-Elmer Co.). Al powder was fed at a rate from 0.5 g/min to 4.0 g/min. Reacting and quenching gas of oxygen were injected into the top of the reactor and the port of quench vessel, respectively. Typical experimental conditions were listed in Table 1. The powders were collected at the reaction tube wall, quench vessel and metal filter, respectively. A vacuum pump was controlled with care because the powder feeder was affected by chamber pressure.

X-ray diffractometer (Model PW 1710, Philips Co.) was used for analysis of the powder compositions. Particle size and size distributions were observed with TEM (Transmission Electron Microscope, JEOL 2000FX-ASID/EDS), SEM (Scanning Electron Microscope, Model 4200, Hitachi) and particle size analyzer (Model SYS 4700, Malvern Instrument Co.).

RESULTS AND DISCUSSION

Chemical equilibrium compositions were calculated by software program based on Gibbs' free energy minimization [Chemsage, ver. 3.2]. Fig. 2 shows the chemical equilibrium plot in Al/O$_2$ system with the molar ratio of 1 to 1. This calculation is
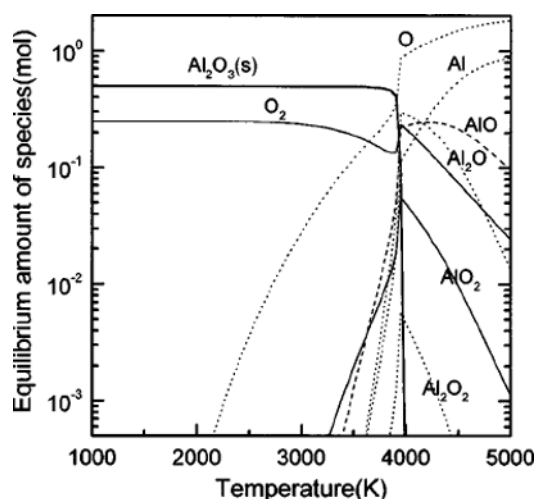
probably not corrected in the low temperature region, especially for solid state materials. However, it is possible to predict the temperature region in which the required species should appear. So, this chemsage program was used for other reaction systems using thermal plasma [Oh and Park, 1998]. As shown in Fig. 2, Al powders were fully vaporized in plasma flame because of its high temperature above 4,000 K. There was rapid reaction of vapor phase Al with oxygen. As the temperature decreased below approx. 4,000 K, the vapor pressure of the species such as Al, AlO, Al$_2$O, AlO$_2$ decreased and there was only Al$_2$O$_3$ species as stable condensed material. It was also observed that the amount of atomic oxygen increased rapidly above 2,300 K; thus, this species would react easily with Al liquid droplet as well as Al vapor. With decreasing the temperature, nucleation due to super-saturation, and subsequent coalescence of Al$_2$O$_3$, would occur under the liquid phase [Ishigaki et al., 1993].

Fig. 3 shows the X-ray diffraction patterns of the powder synthesized in 12 kW of plasma input power without reaction tube. Al powders were fed through the anode nozzle at a rate of 2 g/min. There was not any sharp peak for the powders collected at the wall as shown in (a). This indicated that the particles were not grown enough to form crystalline Al$_2$O$_3$ due to short reaction time. These particles consisted of two forms as shown in Fig. 4. Nano-sized particles with an average diameter of 30 nm resulted from rapid quenching of Al vapor. Whereas, bigger particles with the average diameter of 200 nm resulted from small liquid droplets of Al, which were not fully vaporized Al powders during short residence time in plasma flame.
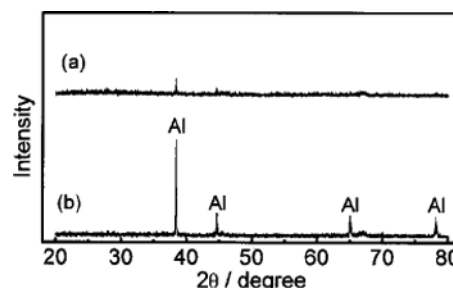

Fig. 3. X-ray diffraction patterns of the powder synthesized without reaction tube.
(a) collected at the chamber wall, (b) collected at the chamber bottom.
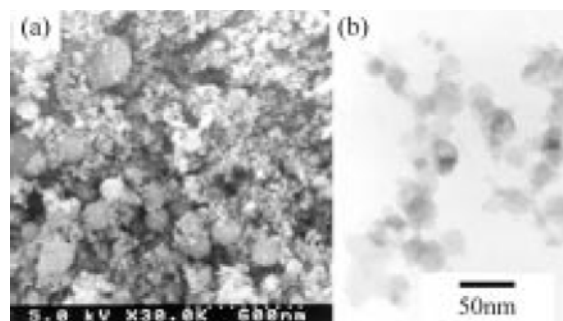

Fig. 2. Chemical equilibrium composition in system of Al/O$_2$ = 1/1.

Fig. 4. Morphology of the powder synthesized without reaction tube.
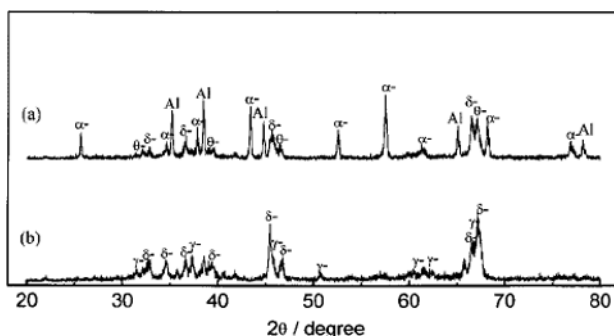(a) SEM photograph, (b) TEM photograph.

Fig. 5. X-ray diffraction patterns of the powder synthesized us-
ing reaction tube.
(a) collected at the reaction tube, (b) collected at the quench
chamber.

The XRD pattern of the powder collected at the bottom of
quench vessel corresponded to Al as shown in Fig. 3(b). There
were sharp peaks of Al due to the powder which were not pro-
perly vaporized and dropped to the bottom of the quench vessel.
These powders were observed to be micro-sized.

To increase the conversion of Al to Al_2O_3, a reaction tube
(length: 400 mm, inside diameter: 45 mm) was attached below
the anode nozzle (torch exit). The plasma flame was constricted
and elongated by the reaction tube, thereby Al powders were
easily vaporized. Fig. 5 shows the x-ray diffraction patterns of
the powder synthesized in 8 kW of plasma input power. The
main peak of the powder obtained at the reaction tube wall
corresponded to α-alumina and other peaks corresponded to Al
and intermediate phase alumina (γ-, δ-, θ-Al_2O_3) in (a). The
powder collected at the quench chamber was observed to the
intermediate phase alumina (γ-, δ-, θ-Al_2O_3) as shown in Fig.
5(b). Homogeneous nucleation during the solidification of liq-
uid droplets of considerable undercooling resulted in the for-
mation of γ-alumina rather than α-alumina because of its lower
critical free energy of nucleation. The powder morphology ob-
served with SEM is shown in Fig. 6. The powders collected at
the reaction tube were composed of nano-sized particle with an
average diameter of 30 nm and some bigger particles with a dia-
meter of 200 nm. Whereas, the powder collected at the quench
vessel, was well distributed with average diameter of 150 nm.

From these results, it was determined that Al powders were
rapidly vaporized in plasma flame, instantaneously reacting with
ambient oxygen to be formed with intermediate phase of Al_2O_3.
These amorphous powders were affected by radiation from pla-
sma flame, so changed to α-phase alumina in reaction tube.
However, a part of the powders was not fully vaporized due to
its short residence time in plasma flame; thus bigger particles de-
posited on the reaction tube wall. The powder collected at the
quench vessel was fully converted to γ- and δ-Al_2O_3. It was de-
termined that vaporization of Al powders was promoted by
elongated plasma flame in the reaction tube and fine Al liquid
droplets rapidly reacted on oxygen, and instantaneously formed
intermediate Al_2O_3.

Fig. 7 shows the X-ray diffraction patterns of the powder
synthesized in 12 kW of plasma input power and heat-treated
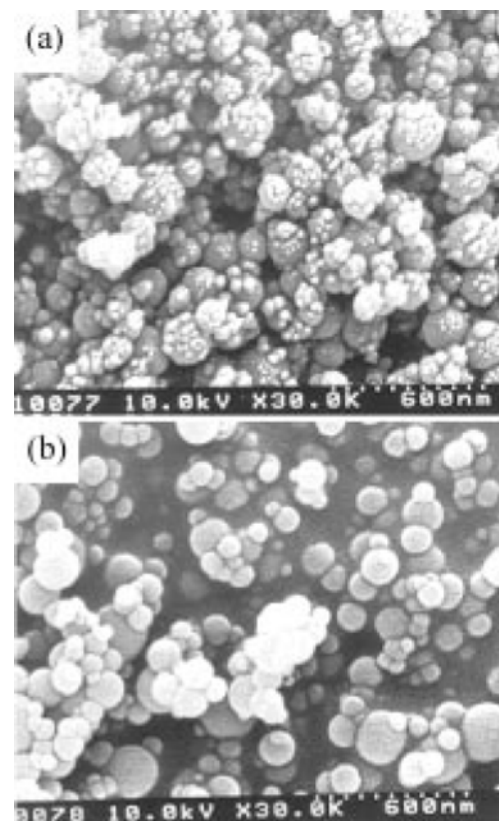for 2 hr. The XRD pattern of the powders collected at the reaction

Fig. 6. SEM photographs of the powder synthesized using re-
action tube.
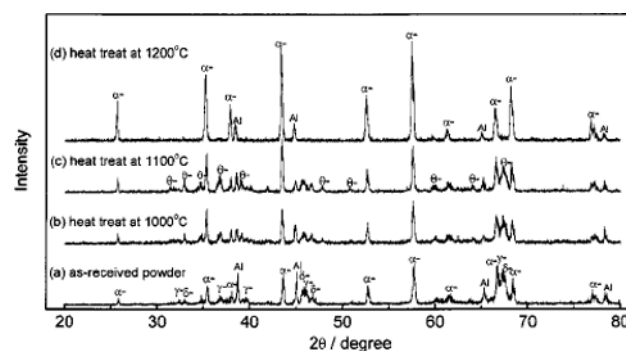(a) collected at the reaction tube, (b) collected at the quench
chamber.

Fig. 7. X-ray diffraction patterns of the powder after heat treat-
ment for 2 hr.

tube indicated that the powders included Al powder as well as
intermediate Al_2O_3 (a). From comparison with Fig. 5(a), plasma
input power did not significantly affect the powder properties.
This should be due to the temperature and velocity of the plasma
stream slightly increasing with the input power. The transforma-
tion of intermediates started at 1,000 °C, which mostly changed
to α-Al_2O_3 at 1,200 °C (d). Most of the Al powders in (a) did
not transform and it was determined that a part of the starting
powder was not vaporized, thus starting Al powders were de-
posited on the reaction tube wall.

Reacting gases were injected through anode nozzle as carrier
of Al powder, top of the reaction tube and quench chamber,

respectively. There was no significant change in different inject-ing positions of reactant gas. From these results, we concluded that the major factor on properties of the powder was the degree of vaporization and quenching condition, which depends on reactor configuration.
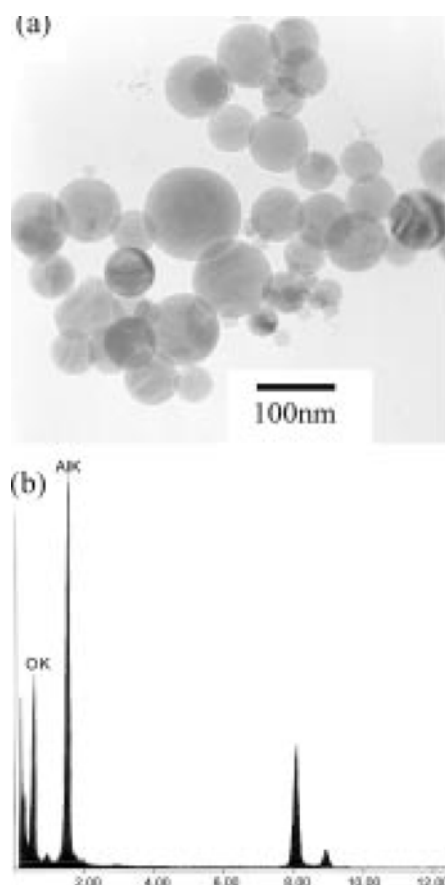

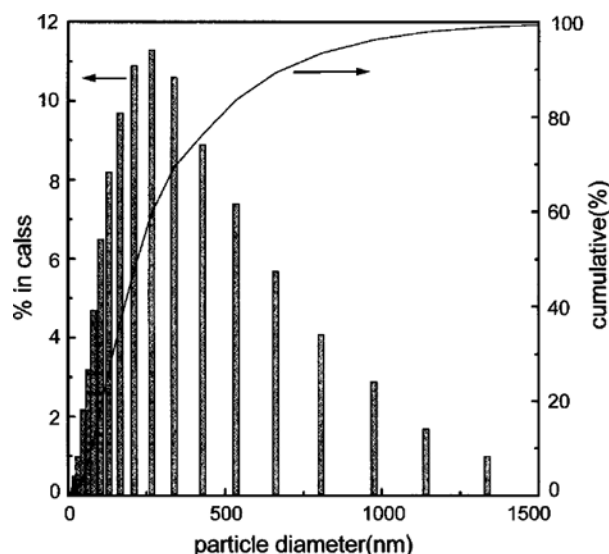**Fig. 8. TEM photograph (a) and EDX analysis (b).**

Fig. 9. Particle size distributions measured by particle size an-alyzer.

Fig. 8 shows the morphology of the power obtained in the quench vessel below the reaction tube by TEM analysis. The average particle diameter was observed with a range from 30 nm to 100 nm in (a). Also, EDX analysis indicated that the powder was composed of 38% of Al and 42% of oxygen as shown in Fig. 8(b). The other peaks were due to carbon coated Cu grid for placing sample powder. Fig. 9 shows particle size distributions of the powder in Fig. 6(a). The average particle diameter was big-ger than the diameter observed from the electron microscope, and it should be due to agglomeration of the powder. Some of the larger particles were due to unevaporated Al powder.

CONCLUSION

Ultra-fine alumina powders were synthesized by using DC thermal plasma. The phase compositions of the powder were mainly affected by reactor configuration. Without a reaction tube, Al powders were not properly vaporized, and nucleation growth was suppressed by rapid quenching. Thereafter, most of the powders were observed to be amorphous Al_2O_3 and some of Al powder. With a reaction tube, the conversion of Al to Al_2O_3 increased the synthesis mechanism as follows: Al pow-ders were rapidly vaporized by elongated plasma flame in the reaction tube. Vapor phase Al species reacted with ambient oxy-gen gas to be formed to intermediate phase of Al_2O_3; thereupon these γ-Al_2O_3 were transformed to α-Al_2O_3 by radiation heat from plasma flame on the reaction tube wall. However, Al pow-ders were not fully vaporized; thus the powders obtained at the reaction tube were from 30 nm to 300 nm. The powders col-lected at the quench chamber were synthesized to the interme-diate phase of Al_2O_3 by rapid quenching. Homogeneous nucle-ation during the solidification of liquid droplets of considerable under-cooling, resulted in the formation of γ-Al_2O_3. These pow-ders were well distributed with average diameter of 150 nm and were white fluffy powders.

ACKNOWLEDGEMENT

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