

# Synthesis and Characterization of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ , $\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{TiO}_2$ Ceramic Composite Particles Prepared by Ultrasonic Spray Pyrolysis

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Fine ceramic particles of zirconia toughened alumina (ZTA), titania toughened alumina (TTA), and zirconia-titania toughened alumina (ZTTA) have been synthesized by ultrasonic spray pyrolysis (USP) at various temperatures from starting salt solutions of various compositions aiming for the development of catalytic material. These particles were characterized for properties such as shape, size and size distribution, diffraction pattern, and chemical and phase composition of elements by scanning electron microscopy (SEM), particle size analyzer (PSA), x-ray diffraction (XRD), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Chemical compositions and sizes of ceramic composites have been controlled by the stoichiometry of salt solutions and the flow rate of spraying solutions. The optimum experimental conditions for the various composite particle syntheses have been proposed.

**Key words :** Ultrasonic spray pyrolysis (USP), Zirconia toughened alumina (ZTA), Titania toughened alumina (TTA), Zirconia-titania toughened alumina (ZTTA), Ceramic composite particle

## Introduction

Ceramics have been widely used as a useful source of industrial and household materials, with the newly developed fine ceramics offering advanced capabilities. Since they are manufactured by well-controlled techniques using highly selected substances, fine ceramics are characterized by finely determined chemical compositions, well-designed structure, and superior properties. They also are superior to metal or organic polymer materials for various functions. Ceramic materials display chemical and thermal stability, electrical insulation, semiconductivity, piezoelectricity, corrosion resistance, and biocompatibility. They also exhibit high dielectricity, chemical adsorption, sound absorption, anti-radioactivity and optical transparency, and are easy to obtain since the main sources of fine ceramics such as alumina ( $\text{Al}_2\text{O}_3$ ), magnesia ( $\text{MgO}$ ), silica ( $\text{SiO}_2$ ) are abundant in the earth. It is noteworthy that combining several different ceramic materials can create a material with new capabilities which produces ceramic composite material. This is particularly important since a thermally resistant material of ceramic composite material can substitute for the super metal alloys of Ni, Cr, and Co, which are being used for the purpose of thermal resistance and mechanical strength. Therefore, ceramic materials can now be used to minimize metal usage.<sup>1</sup>

Among the fine ceramics, alumina has a variety of applications. It is used as sources for IC boards, IC packaging, and other industrial materials due to its electrical insulation and magnetic properties. Alumina's chemical composition also makes it useful as a catalyst or a catalytic support.

Zirconia is the third most widely used ceramic material after alumina and silica. It is a good source for structural material because of its physical and mechanical characteristics.

It displays piezoelectricity, semiconductivity, and ionic conductivity, making it useful for oscillators, thermistors, and oxygen sensors. Its high melting point and resistance to corrosion allows zirconia to be used as a source for fireproof materials or materials used in high temperature chemical processes.

Titania is used as sources for porcelain, polishing agent, medicine and cosmetics, and recently for optical catalysts and oxygen sensors that control the air/fuel ratio in automobiles. The synthesis of spherically-shaped powder is strongly required for the fabrication of these devices.

It has been of interest to combine the characteristic properties of these single ceramic material to a composite material. Ultrasonic spray pyrolysis that we employed in this study is a good technique to prepare spherically-shaped fine particles. In this technique, fine liquid droplets were formed from a starting salt solution using an ultrasonic oscillator, which then were changed to ultrafine particles through pyrolysis in a high temperature reaction furnace. This method produces fine spherically-shaped particles with a uniform size distribution, and especially in this case, each of the liquid droplets of the starting solution acts as a small reactor which can confine the inequality of particle composition on that spherical secondary particle. This method is also an easy and reproducible way to control the size distribution of particles as a function of concentration. Spray pyrolysis system can be divided into three main parts: sonicator which can generate fine liquid droplets, pyrolysis furnace of liquid droplets, and collector of the synthesized particles.

Kim *et al.*<sup>2</sup> prepared  $\text{TiO}_2$  and  $\text{BaTiO}_3$  powder by ultrasonic spray pyrolysis from metal alkoxide solution in the temperature range of 400-900 °C with a resonance frequency of 1.6 MHz and collected the powder with glass filters. The primary particles prepared by this method were

about 0.02  $\mu\text{m}$  in size. Their sizes were independent of pyrolysis temperature, but increased and then decreased with increasing concentration of salt solution.

V. Jokanovic *et al.*<sup>3</sup> prepared high temperature ultrafine particles of  $\alpha$ -alumina from a starting solution of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The droplet size was about 0.3  $\mu\text{m}$  and particle size was smaller than that in the present study. The shape of the fine particles produced was almost the same as that of the liquid droplets. The fine particles of alumina synthesized undergo phase transition in the temperature range of 1073-1173 K.

Chii-Shyang *et al.*<sup>4</sup> prepared ZTA powders containing more than 5.5 mol % of  $\text{TiO}_2$  additive by hot-pressing for 1 hour at 1350  $^\circ\text{C}$ . They reported that the bending strength and hardness of ZTA improved as the amount of  $\text{TiO}_2$  increased.

Han *et al.*<sup>5</sup> produced alumina toughened zirconia (ATZ) by the alumina coating method and reported that they obtained ATZ with a relative density of higher than 99% by sintering the sample for 2 hours in the temperature range of 1450-1550  $^\circ\text{C}$ . They also showed that ATZ containing 20 wt% alumina represented 8  $\text{MPa}/\text{m}^{1/2}$  of breaking strength ( $K_{\text{IC}}$ ), which is higher than 6  $\text{MPa}/\text{m}^{1/2}$  obtained by the ball mill method.

In this study, ultrasonic spray pyrolysis method was employed to prepare ceramic composite particles of zirconia toughened alumina (ZTA), titania toughened alumina (TTA) and zirconia-titania toughened alumina (ZTTA) aiming for the development of catalytic material. The prepared fine particles have been characterized by various techniques and the effects of the concentration of solution, pyrolysis temperature, and reaction time on the properties of ceramic composite particles were investigated. The optimum experimental condition for the preparation of ceramic fine particles were also investigated.

## Experimental Section

**Preliminary Work for Single Materials.** Fine particles of pure alumina and  $\text{ZrO}_2$  were synthesized and analyzed prior to our composite material of ZTA by ultrasonic spray pyrolysis. The results of characteristic analyses for alumina and  $\text{ZrO}_2$  were used as basis data for the work. We synthesized alumina particles from 0.1 M of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 7:3 water/ethanol mixed solvent at the drying zone temperatures of 400-550  $^\circ\text{C}$ , at pyrolysis temperatures of 850, 900, 950, 1000, and 1100  $^\circ\text{C}$ , which were dried at 100  $^\circ\text{C}$  for more than 2 hours and were analyzed. According to the XRD analysis, we observed the characteristic peaks corresponding to the  $\gamma$ - $\text{Al}_2\text{O}_3$  at all temperature ranges used in the experiment, which was more distinct at a higher temperature. However, at temperatures higher than 1100  $^\circ\text{C}$ , new peaks showed up, which is assigned to the formation of  $\alpha$ - $\text{Al}_2\text{O}_3$ , consistent with the results reported by other group.<sup>6-9</sup>

For  $\text{ZrO}_2$ , powders were produced through pyrolysis of 0.056 M aqueous solution of  $\text{ZrCl}_2\text{O} \cdot 8\text{H}_2\text{O}$  (Junsei, Japan, CP) at 950 and 1050  $^\circ\text{C}$ . They were then collected and dried

at 110  $^\circ\text{C}$  for 2 hours and analyzed with various techniques.

**Preparation of Starting Solutions.** Water soluble salts of zirconium, titanium, and aluminum were used as cation supplies. The starting materials were the aqueous solution of each salt with a concentration of 0.05-0.1 mol/l.  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Duksan, Korea, FG) or  $\text{AlCl}_3$  (Duksan, Korea, FG) was used as a supply of aluminum cation,  $\text{ZrCl}_2\text{O} \cdot 8\text{H}_2\text{O}$  (Junsei, Japan, CP) for zirconium cation, and  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  (Aldrich, USA, 99.999%) for titanium cation. The starting solutions were prepared by dissolving precursors in distilled water in corresponding amount.

The  $\text{ZrO}_2$  contents of ZTA were varied from 5% to 15% in every 5% and the  $\text{TiO}_2$  contents of TTA were varied to 2.5%, 5% and 10%. The  $\text{TiO}_2$  contents of ZTTA were varied in the range of 1.5-7.5 wt% with the fixed amount of 15 wt%  $\text{ZrO}_2$  so that the  $\text{Al}_2\text{O}_3$  contents were resulted in the range of 77.5-83.5 wt%. According to the amount of  $\text{TiO}_2$  contained, they are denoted as ZTTA-1 (1.5 wt%), ZTTA-2 (3 wt%), ZTTA-3 (4.5 wt%), ZTTA-4 (6 wt%), and ZTTA-5 (7.5 wt%) respectively.

Since  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  can precipitate to  $\text{TiO}_2$  by reacting with water at room temperature, it is necessary to dissolve  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  solution in 100 mL of absolute ethanol first and then adjust the concentration of salt solution with distilled water to avoid the precipitation problem.

**Apparatus of Ultrasonic Spray Pyrolysis.** Figure 1 shows the apparatus of ultrasonic spray pyrolysis. It consists mainly of three parts, which are sprayer, pyrolysis furnace, and collector. The ultrasonic sprayer with resonant frequency of 1.6 MHz employed was a modified apparatus of general household ultrasonic humidifier (Daewoo, KH-3550, Korea), which was connected to a reaction tube of the furnace. While the sprayed liquid droplets generated from ultrasonic sprayer were passing through reaction tube, they undergo heating, solvent evaporation, pyrolysis, reaction with oxygen in the air, and finally form fine ceramic particles.

The reaction furnace was divided into two zones, one is a drying zone with a temperature range of 400-550  $^\circ\text{C}$ , and the

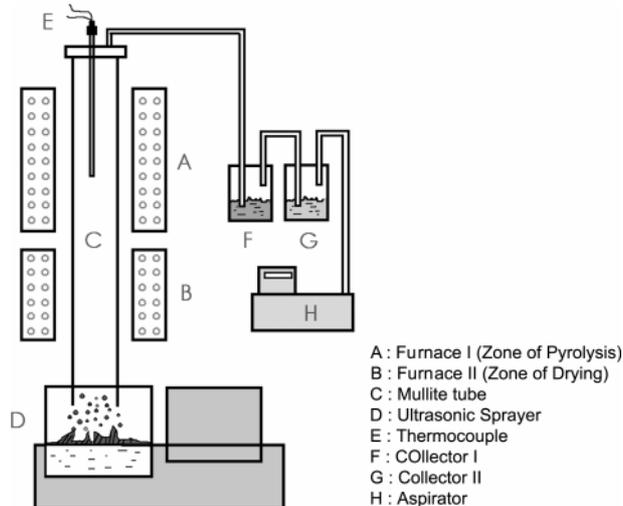


Figure 1. Schematic diagram of ultrasonic spray pyrolysis system.

other is a pyrolysis zone with a temperature range of 850-1400 °C. By running the experiment with the temperature gradient in these zones, it was possible to overcome the problem of producing irregular shaped particles which arised from a sudden heating and a rapid solvent evaporation occurred in a single temperature systems. Thus spherical fine particles could be generated. The material of the reaction tube (ID = 5 cm, L = 150 cm) was mulite and the temperature was measured by an external digital thermometer in the drying zone, and by an internal thermocouple in the pyrolysis zone. The temperature in the drying zone was adjusted to be 50% of that in the pyrolysis zone, that is, the temperature of powder synthesis.

Fine particles were collected into a container containing distilled water by wet method. There were two collectors installed and most of the fine particles were collected by the first collector. The collected fine particles were dried at 110 °C for 2 hours.

In the preparation of 5 wt% ZTA particles, ZTA was synthesized by raising the pyrolysis temperature by 50 °C in the range of 850-1100 °C, and also at 1200 °C, while for 10 wt% and 15 wt% ZTA's, the particles were synthesized by raising the pyrolysis temperature by 50 °C or 100 °C in the range of 900-1400 °C. The particles produced in this way were collected and dried at 110 °C for 2 hours and then characterized.

In the case of TTA powder, 5 wt% and 10 wt% samples were able to be sprayed, while 15 wt% sample was not, due to its high viscosity. We thus synthesized 2.5 wt% TTA in order to have the information about the general tendency. If Ti ion is included in aquous solution, it forms oxydized precipitates at room temperature. Therefore, the reaction solution needed to be cooled in order to keep the solution from the formation of precipitates. In our spray experiment, we tried to avoid the formation of precipitates by spraying the solution within a small amount at a time, and each time the solution was freshly made. The powder produced in this way was also dried at 110 °C for 2 hours and then analyzed.

ZTTA powder was synthesized in a manner similar to that of other cases.

**Particle Analyses.** The method of thermogravimetry (TG, SHIMADZU, DS-50, Japan) was used to determine the temperatures of pyrolysis and crystallization for the synthesized powder with the heating rate of 10 °C/min up to 1400 °C in a N<sub>2</sub> atmosphere. The phase analysis was performed by using X-ray diffractometer (MAC, MOXHF, Japan) with a scanning speed of 5.0 deg/min in the range of 10° < 2θ < 90°. We also used the particle size analyzer (SHIMADZU, SA-CP3, Japan) to get the information of average size, surface area and size distribution for the particles, SEM (Jeol, JSM-5400, Japan) for the size and the shape, ICP-AES (JY50P, Jobin Yvon, France) for the ingredients of particles.

## Results and Discussion

**Characterization of ZTA Fine Particles.** We synthesized zirconia toughened alumina (ZTA) through ultrasonic spray

pyrolysis. We varied the content of ZrO<sub>2</sub> to be 5, 10, and 15 wt%. It was reported<sup>11</sup> that in the synthesis of ZTA using emulsion spray hydrolysis, the mass ratio of Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> was adjusted to be 80/20, because in this condition the amount of square-shaped ZrO<sub>2</sub> becomes a maximum at room temperature and also with this ratio, ZTA exhibits maximum fracture strength.

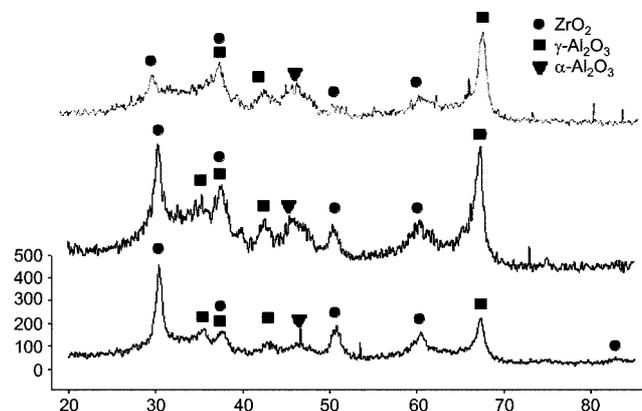
The ZTA particles containing 5 wt% of ZrO<sub>2</sub>, which was prepared through pyrolysis of 0.16M AlCl<sub>3</sub>/ZrCl<sub>2</sub>O · 8H<sub>2</sub>O, shows distinct XRD peaks of γ-alumina but does not show the characteristic peaks which show the existence of ZrO<sub>2</sub> clearly at low temperature (850 °C). However, above 950 °C, the characteristic peaks of ZrO<sub>2</sub> become sharp, which means that in the preparation of ZTA particles, the reaction temperature needs to be set above 950 °C, and this is the same for the case of 10 wt% of ZrO<sub>2</sub>, too.

For ZTA particles containing 15 wt% of ZrO<sub>2</sub>, the characteristic peaks of both alumina and zirconia appeared in the temperature range of 900-1400 °C. It was found from the XRD results of 5, 10, 15 wt% ZTA that, as the amount of zirconia increases, the temperature of showing ZTA peaks became higher.

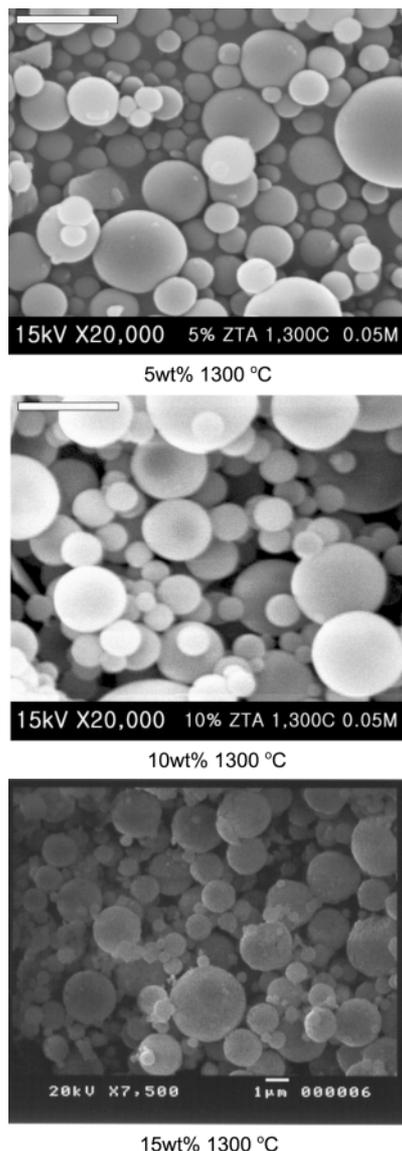
In Figure 2, the X-ray diffraction patterns of ZTA powders containing 5, 10, and 15 wt% of ZrO<sub>2</sub>, which were prepared from AlCl<sub>3</sub>/ZrCl<sub>2</sub>O · 8H<sub>2</sub>O with pyrolysis temperature of 1200 °C, are shown. The characteristic peaks of α-Al<sub>2</sub>O<sub>3</sub> in X-ray diffraction pattern start to appear above 1200 °C, which is the temperature of phase transition of γ-form to α-form. Therefore, in ultrasonic spray pyrolysis, it would be possible to synthesize α-Al<sub>2</sub>O<sub>3</sub> powders above 1200 °C without any further process.

Figure 3 is the SEM photographs of ZTA containing 5, 10, and 15 wt% of ZrO<sub>2</sub>, which show that the particles synthesized above 1300 °C are fine, as small as 1-2 μm in size, spherically-shaped, and do not show coalescing phenomena which were shown at lower temperature.

In Table 1, the particle size distributions of the above samples synthesized at 1200 °C through pyrolysis are listed. The mean diameter of the particle was determined to be



**Figure 2.** X-ray diffraction patterns of as-prepared ZTA powder by ultrasonic spray pyrolysis at 550 °C drying zone and 1200 °C pyrolysis zone with AlCl<sub>3</sub>/ZrCl<sub>2</sub>O · 8H<sub>2</sub>O aqueous solution (bottom: 15 wt%, middle: 10 wt%, top: 5 wt%). ● ZrO<sub>2</sub>, ■ γ-Al<sub>2</sub>O<sub>3</sub>, ▼ α-Al<sub>2</sub>O<sub>3</sub>



**Figure 3.** SEM photographs of as-prepared ZTA powder by ultrasonic spray pyrolysis at 550 °C drying zone and various temperature of pyrolysis zone with  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{ZrCl}_2\text{O} \cdot 8\text{H}_2\text{O}$  aqueous solution.

**Table 1.** Particle size distributions of as-prepared ZTA powder by ultrasonic spray pyrolysis

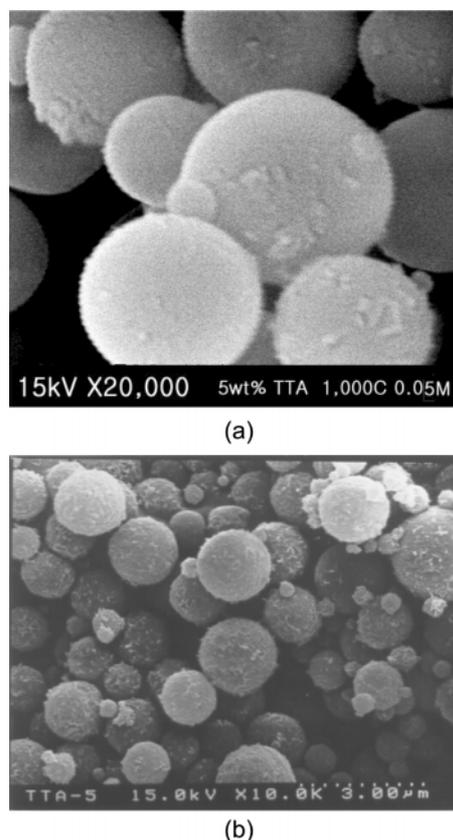
Sample	Median Diam. ( $\mu\text{m}$ )	Surface Area ( $\text{m}^2/\text{g}$ )	Modal Diam. ( $\mu\text{m}$ )	Standard Deviation ( $\mu\text{m}$ )
5% ZTA	1.47	1.913	1.58	0.078
10% ZTA	1.32	2.043	1.28	0.111
15% ZTA	1.03	1.979	1.11	0.183

about 1.3  $\mu\text{m}$ , regardless of the amount of  $\text{ZrO}_2$  contained, but the modal diameter decreases and particle size distributions are narrowed as the amount of  $\text{ZrO}_2$  increases. It is estimated that the lattice size of  $\text{ZrO}_2$  is less than that of  $\text{Al}_2\text{O}_3$ .

Table 2 lists the result of elemental analysis by ICP-AES

**Table 2.** ICP-AES data of as-prepared ZTA powder by ultrasonic spray pyrolysis

Sample	Elements	5%	10%	15%
		Con (ppm)	Con (ppm)	Con (ppm)
950 °C	Al / Zr	63.2 / 10.7	407 / 87.8	-
1000 °C	Al / Zr	98.7 / 12.3	232 / 87.9	295 / 130
1050 °C	Al / Zr	79.4 / 12.1	277 / 81.7	250 / 132
1100 °C	Al / Zr	98.9 / 11.5	148 / 88.4	179 / 134
1150 °C	Al / Zr	-	401 / 85.9	281 / 133
1200 °C	Al / Zr	92.7 / 11.4	109 / 87.5	300 / 128



**Figure 4.** SEM photographs of as-prepared TTA powder by ultrasonic spray pyrolysis at 500 °C of drying zone and 1000 °C temperature of pyrolysis zone with  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  aqueous solution. a) 5 wt% TTA powder ( $\times 20,000$ ) b) ( $\times 10,000$ ).

method for ZTA particles. As are shown, the compositions of each wt% of ZTA particles were a little different from what we calculated and estimated in the preparation of starting solution. For example, for the ZTA particles which we prepared to be 5 wt% of zirconia, we obtained about 15 wt% of Zr at temperature of lower than 1000 °C, and about 10 wt% of Zr at temperature of higher than 1000 °C.

For 10 and 15 wt% samples, this deviation becomes large. However, in terms of the amount of Zr simply, there is a certain rate of increment of Zr content from 5 to 10, 15 wt%. Another thing is, the powders synthesized at temperatures of higher than 1000 °C show a stable amount of  $\text{ZrO}_2$  contained.

**Analysis of TTA Fine Particles.** Even though there is an example of preparation of  $\text{TiO}_2$  powders through ultrasonic

spray pyrolysis using aqueous solution of  $\text{TiCl}_4$  as a source, there was no evidence of TTA synthesis through this technique. In this experiment, similar to the case of ZTA, we prepared titania toughened alumina containing 5, 10, and 15 wt% of titania. Unfortunately, since the samples of TTA containing more than 10 wt% of Ti cation had difficulties to be sprayed due to the increase of viscosity, we excluded 15 wt% TTA powders from a characteristic analysis.

Figure 4 shows the SEM photographs of 5 wt% of TTA which was synthesized through pyrolysis using mixed solution of 0.05 M and 0.075 M of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ . The prepared fine particles are represented to be spherical in shape as are shown in the photographs even though there are some traces of broken particles or particles with empty cores. The size of the particles were measured to be about  $2 \mu\text{m}$  while their size distribution was not uniform.

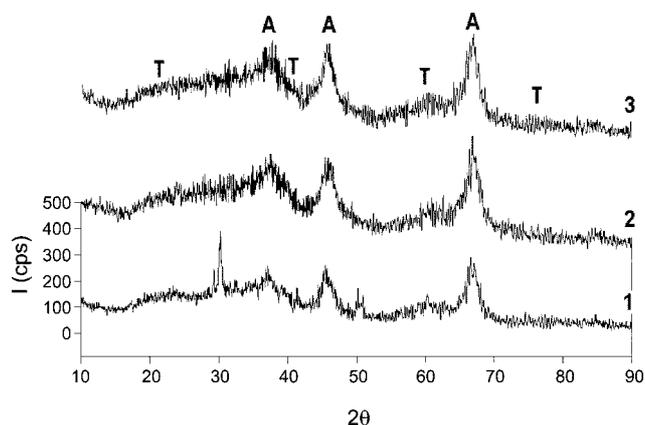
According to the result of size analysis of 2.5, 5, 10 wt% of TTA particles shown in Figure 5, which were synthesized through  $1000^\circ\text{C}$  pyrolysis using 0.05 M of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , the particles show a relatively narrow distribution with a median diameter of 0.7-1.2  $\mu\text{m}$ . The result of elemental analysis of particles using ICP-AES technique reveals different compositions from what we estimated, as was the case in ZTA. The evaluated amount of Ti contained in TTA particles synthesized at  $850^\circ\text{C}$  was 5.42 wt%, which was close to what we estimated, but that in TTA particles synthesized at  $1000^\circ\text{C}$  was far from what we expected. The deviation of this experimental result in high temperature was not properly understood.

In Figure 6, the X-ray diffraction patterns of TTA powders containing 2.5 wt%, 5 wt%, and 10 wt% of  $\text{TiO}_2$ , which were prepared from  $\text{AlCl}_3/\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  with pyrolysis temperature of  $1000^\circ\text{C}$ , are shown. As shown in the figure, the characteristic peaks of  $\text{TiO}_2$  in X-ray diffraction pattern appears as a small scale in the 5 wt% of  $\text{TiO}_2$  and it grows more and more as the contents of  $\text{TiO}_2$  increase, which shows the corresponding ratio of  $\text{TiO}_2$  in TTA powders.

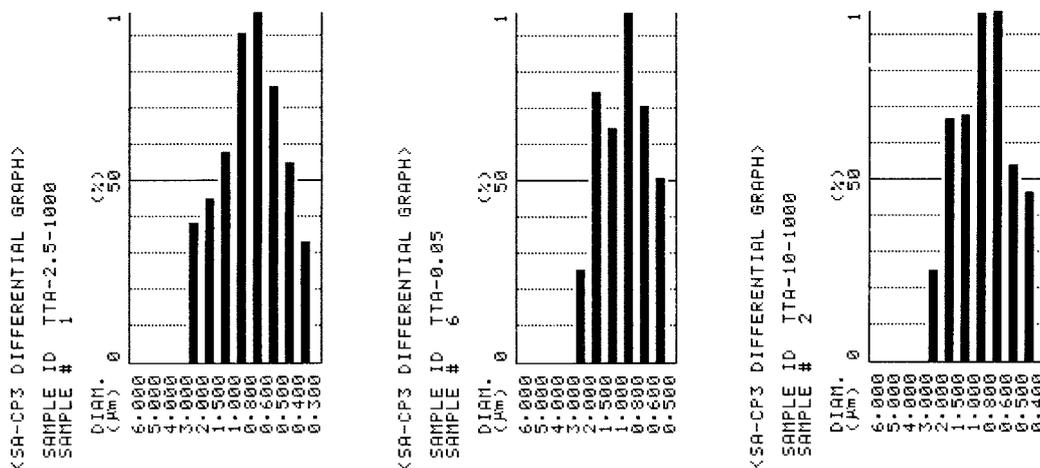
**Analysis of ZTTA Fine Particles.** Since we had experienced

synthesizing fine particles containing additives such as ZTA and TTA using ultrasonic spray pyrolysis, it is tried to add zirconia and titania together into alumina. So far, the technique used to synthesize these 3 kinds of composite powders, ZTA, TTA, and ZTTA, was mostly a direct mixing of separately produced powders by hot pressed method, thus the method that we use is very convenient way for the preparation of spherical fine particles of these ceramic composites.

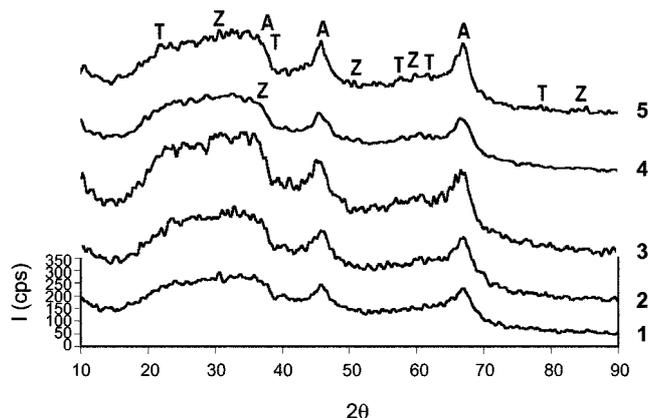
In this study, we fixed the content of zirconia to be 15 wt%, and increased the content of titania by small amount from 1.5 wt% to 7.5 wt% in order to prepare the mixed solution of 0.05 M, 0.075 M, and 0.1 M of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , and synthesized ZTTA particles through pyrolysis at  $1000^\circ\text{C}$ . For the ZTTA particles produced through  $1000^\circ\text{C}$  pyrolysis from 0.05 M mixed solution, It was able to observe the characteristic diffraction patterns for  $\gamma$ -alumina and zirconia, but not for titania, as is shown in Figure 7. This may due to the fact that the peak position of titania is near those of alumina and zirconia, and also the



**Figure 6.** X-ray diffraction patterns of as-prepared TTA powder by ultrasonic spray pyrolysis at  $500^\circ\text{C}$  drying zone and  $1,000^\circ\text{C}$  pyrolysis zone with 0.05 M mixed aqueous solution. A and T indicates the characteristic peaks of  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  respectively. (1: 2.5 wt% TTA, 2: 5 wt% TTA, 3: 10 wt% TTA)



**Figure 5.** Particle size distributions of as-prepared TTA powder by ultrasonic spray pyrolysis at  $500^\circ\text{C}$  drying zone and  $1000^\circ\text{C}$  pyrolysis zone with 0.1 M  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  aqueous solution. (1: 2.5 wt%, 2: 5 wt%, 3: 10 wt%)



**Figure 7.** X-ray diffraction patterns of as-prepared ZTTA powder by ultrasonic spray pyrolysis at 500 °C drying zone and 1,000 °C pyrolysis zone with 0.05 M mixed aqueous solution. A, Z and T indicate the characteristic peaks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> respectively. (1: ZTTA-1, 2: ZTTA-2, 3: ZTTA-3, 4: ZTTA-4, 5: ZTTA-5).

amount of titania is relatively low.

The results of ICP-AES elemental analysis listed in Table 4 tell us that the amount of alumina was lower than what we estimated, on the other hand, the amount of zirconia (which we fixed the quantity) was more than we added. The amount of titania was also a little bit more than we added. Adjusting the amount of titania to be 3 wt% seemed to be a reasonable condition for the preparation of ZTTA to have desired compositions.

The deviation of the real amount of each component from what we calculated in the first place, which happened commonly in most cases, is the problem necessary to be improved in this ultrasonic spray pyrolysis.

In Figure 8, the SEM photographs of ZTTA synthesized through 1000 °C pyrolysis from 0.075 M mixed solution are shown. Similarly to what is observed in ZTA cases, most of the ZTTA particles containing 1.5 to 6 wt% of titania are spherical in shape, and are fine in size even if they do not have a uniform distribution. However, the ZTTA particles synthesized at 1000 showed a significant coalescing of

particles and a production of particles with empty cores. The reason for this is that there may be a rapid pyrolysis in the surface and also inside the solution at the same time due to the heat evolved from mixing alcohol with water, and can be improved by adjusting the synthetic temperature and the condition of pyrolysis such as a residence time, etc.

Table 5 provides the data for size distribution of ZTTA synthesized at 1000 °C pyrolysis using 0.05 M mixed solution. The size of ZTTA particles becomes larger as the amount of TiO<sub>2</sub> increases and as that of Al<sub>2</sub>O<sub>3</sub> decreases, and the surface area of particles follows the same tendency. This is an opposite trend to that of ZTA, where the particle size became smaller with the amount of zirconia increasing. The size distribution is wide as was shown in SEM photographs.

## Conclusions

The fine particles of zirconia toughened alumina (ZTA), titania toughened alumina (TTA) and zirconia-titania toughened alumina (ZTTA) were synthesized through ultrasonic spray pyrolysis at various concentrations and temperatures. The prepared particles were collected by wet process and analyzed to investigate the following characteristic properties by XRD, PSA, SEM, and ICP-AES techniques after being dried.

The particle sizes and size distributions of produced ZTA and ZTTA particles were able to be controlled as a function of experimental condition such as the reaction temperature, solvent, concentration of solution, the power of oscillator, etc.

ZTA particles were difficult to be synthesized at lower temperature, while above the temperature of 1000 °C, good crystalline particles were produced. As the temperature went up, spherically-shaped fine particles with a narrow size distribution were generated. The amount of ZrO<sub>2</sub> in ZTA particles were examined to be higher than 5-15 wt% of estimated values. The median diameter of the particles was found to be about 1.376  $\mu$ m and the average surface area was measured to be 1.978 m<sup>2</sup>/g.

For TTA particles, even if there were some broken parts or empty parts observed, most of the particles were shown as

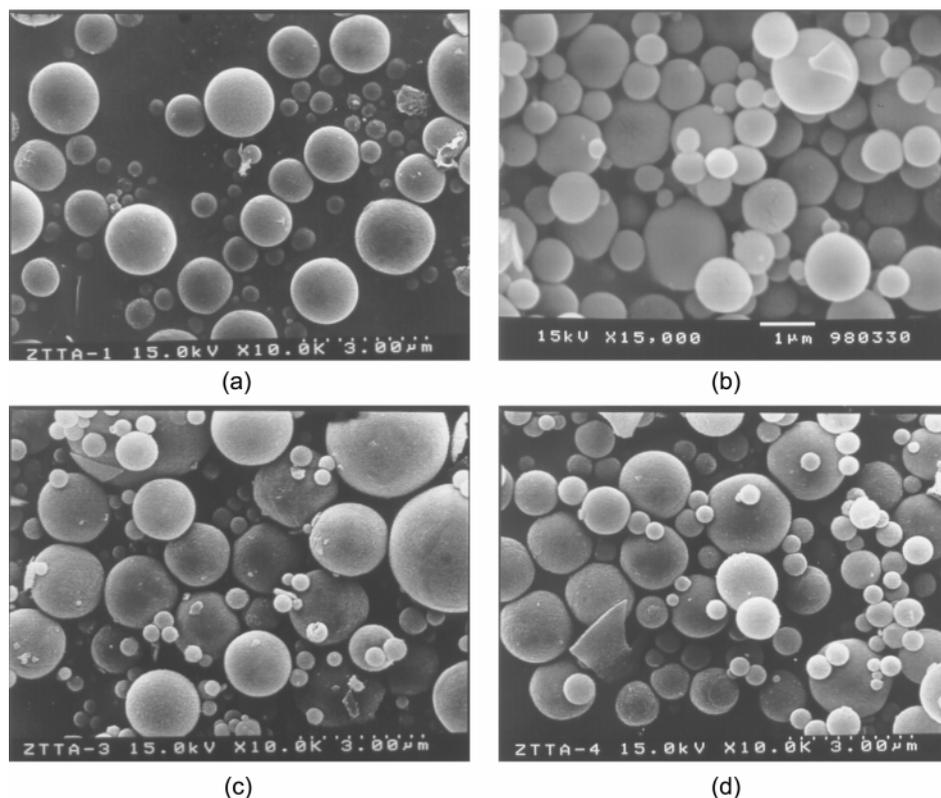
**Table 3.** Particle size distributions of as-prepared TTA powders by ultrasonic spray pyrolysis

Sample	Median Diam. ( $\mu$ m)	Surface Area (m <sup>2</sup> /g)	Modal Diam. ( $\mu$ m)	Concentration ( $\mu$ m)	Standard Deviation ( $\mu$ m)
2.5 wt% TTA	0.82	2.175	0.72	1.0	0.086
5 wt% TTA	0.96	2.040	1.22	0.05	0.121
10 wt% TTA	0.89	2.110	0.74	0.05	0.167

**Table 4.** ICP-AES data of as-prepared ZTTA powder by ultrasonic spray pyrolysis

(unit : wt%)

Samples	Calculated Value			0.05 M			0.075 M			0.1 M		
	Al	Zr	Ti	Al	Zr	Ti	Al	Zr	Ti	Al	Zr	Ti
ZTTA-1	83.5	15	1.5	77.13	20.81	2.06	76.09	22.23	1.71	72.53	25.16	2.31
ZTTA-2	82	15	3	73.98	22.88	3.12	71.06	24.99	4.05	75.13	21.63	3.24
ZTTA-3	80.5	15	4.5	71.88	23.06	5.06	71.89	22.68	5.43	71.08	23.57	5.35
ZTTA-4	79	15	6				72.51	21.08	6.41			



**Figure 8.** SEM photographs of as-prepared ZTTA powder by ultrasonic spray pyrolysis at 500 °C drying zone and 1000 °C temperature of pyrolysis zone with 0.075 M  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} / \text{ZrCl}_2\text{O} \cdot 8\text{H}_2\text{O} / \text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  aqueous solution. a) ZTTA-1, b) ZTTA-2, c) ZTTA-3, d) ZTTA-4.

**Table 5.** Particle size distributions of as-prepared 0.05 M ZTTA powder by the ultrasonic spray pyrolysis

Sample	Median Diam. ( $\mu\text{m}$ )	Surface Area ( $\text{m}^2/\text{g}$ )	Modal Diam. ( $\mu\text{m}$ )	Standard deviation ( $\mu\text{m}$ )
ZTTA-1	1.08	3.755	1.25	0.836
ZTTA-2	0.93	3.818	0.92	0.357
ZTTA-3	0.70	3.518	0.74	0.167
ZTTA-4	0.77	3.193	0.78	0.168
ZTTA-5	0.70	2.884	0.74	0.090

spherical in shape. In the preparation of TTA particles containing higher than 10 wt% of titania, improved condition of synthetic process is required, because the viscosity of solutions containing higher than 10 wt% of titania is so high to be easily sprayed. The particles produced were fine and spherically-shaped with the average size smaller than 2  $\mu\text{m}$ .

ZTTA particles synthesized were fine and spherically-shaped, and the median diameter of smaller than 1  $\mu\text{m}$  and surface area of 3.434  $\text{m}^2/\text{g}$  were determined. The analyzed contents of alumina in ZTTA's were found to be lower than the estimated values, that of zirconia was a little higher than the estimated value, while that of titania was close to the estimated value.

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