

Characterization of Zirconia-Toughened-Alumina Composite Powder Synthesized by Spray Pyrolysis Technique

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Zirconia-toughened-alumina powders containing up to 40 wt% ZrO_2 have been synthesized by spray pyrolysis of nitrate solutions to examine the particle structure and the crystallization behavior using a transmission electron microscope, X-ray diffraction and a differential thermal analysis. As-prepared powders were composed of fine and hollow spherical particles of very thin film showing non-crystalline phase. When they were calcined, tetragonal ZrO_2 began to crystallize during η - Al_2O_3 - θ - Al_2O_3 conversion around 1000-1100 °C and transformation to α - Al_2O_3 occurred around 1100-1200 °C. The crystallization of aluminas was markedly inhibited by ZrO_2 contained. The ZrO_2 grains existed as very fine single crystals uniformly dispersed within α - Al_2O_3 grains and conserved the tetragonal form even after calcining at 1400 °C.

Key word: zirconia-toughened-alumina composite powder, spray pyrolysis, particle structure, crystallization behavior

1. INTRODUCTION

It has been well recognized that the reproducible preparation of pure and homogeneous reactive powders is the key step in processing of advanced ceramics. Hence, a great number of chemically and/or physically controlled techniques of preparing the raw powders has been researched, including spray pyrolysis, sol-gel, coprecipitation, hydrothermal processes, and so on.¹ Among the many techniques, the more complex become the powder systems, the larger amount of attention has been receiving the spray pyrolysis method² because of its several advantages, permitting easy running, such as one-step process, very short processing time, and capability of continuous synthesis compared to the other methods. We have recently studied the powder preparation by the spray pyrolysis method for several kinds of multicomponent oxide systems such as Y_2O_3 -doped ZrO_2 ,³ $BaTiO_3$,⁴ and PLZT.⁵ In the present work, this method has been applied to the synthesis of zirconia-toughened-alumina (ZTA) powders.

ZTA ceramics⁶ have high fracture toughness and strength due to microcrack and stress-induced transformation of tetragonal ZrO_2 to monoclinic ZrO_2 during fracturing process. Accordingly, it is necessary to retain the tetragonal form as a metastable phase in the sintered bodies at room temperature during fabrication.⁷ For this purpose decreasing ZrO_2 grain size is recognized to be available. It is also well demonstrated that toughening is enhanced by increasing the uniformity of zirconia dispersion.⁸

As-prepared ZTA powders by the spray pyrolysis technique revealed non-crystalline phase.⁹ By the following calcination, however, uniformly dispersed fine grains of tetragonal ZrO_2 precipitated in α - Al_2O_3 matrix grains. In this paper, the changes in the particle

structure and crystalline phases are reported.

2. EXPERIMENTAL

The stock solutions were prepared by dissolving $Al(NO_3)_3 \cdot 9H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ into water / alcohol (13 vol% methanol and 86 vol% ethanol) of volumetric ratio = 1 / 1 to yield $ZrO_2 / (ZrO_2 + Al_2O_3) = 0-40$ wt% powder after the salts fully decomposed. The solution concentration was adjusted to $[Al^{3+} + Zr^{4+}] = 0.5$ mol/l. The spray pyrolysis apparatus used in this study was the same as described before.³ Some synthetic conditions were fixed as follows; furnace temperature: 800 °C, solution feed rate: 2.5-3 ml/min, atomizer air pressure: 90 KPa and atomizer air feed rate: 3.0-3.5 l/min.

Samples of the spray-pyrolyzed powders were placed in Al_2O_3 crucibles and calcined at 700-1400 °C for 1h. The crystalline phases in each powder were determined before and after the calcination using X-ray diffraction (XRD). The crystallization temperatures of η - and α - Al_2O_3 in samples were analyzed by a differential thermal analysis (DTA). The particle structure of the samples was observed by a transmission electron microscope (TEM) equipped an energy-dispersive X-ray analyzer (EDX) at an accelerating voltage of 300 kV.

3. RESULTS AND DISCUSSION

As-synthesized powders ($ZrO_2 = 0-40$ wt%) showed non-crystalline phase by XRD regardless of their ZrO_2 contents. Contrarily, as-prepared powders of pure ZrO_2 by the similar manner revealed a tetragonal structure. Sproson and Messing¹⁰ prepared Al_2O_3 -15 vol% ZrO_2 powders by the modified spray pyrolysis method using a slurry of α - Al_2O_3 powder dispersed in a solution of $ZrO(NO_3)_2$ as a atomizing material. ZrO_2 in the as-

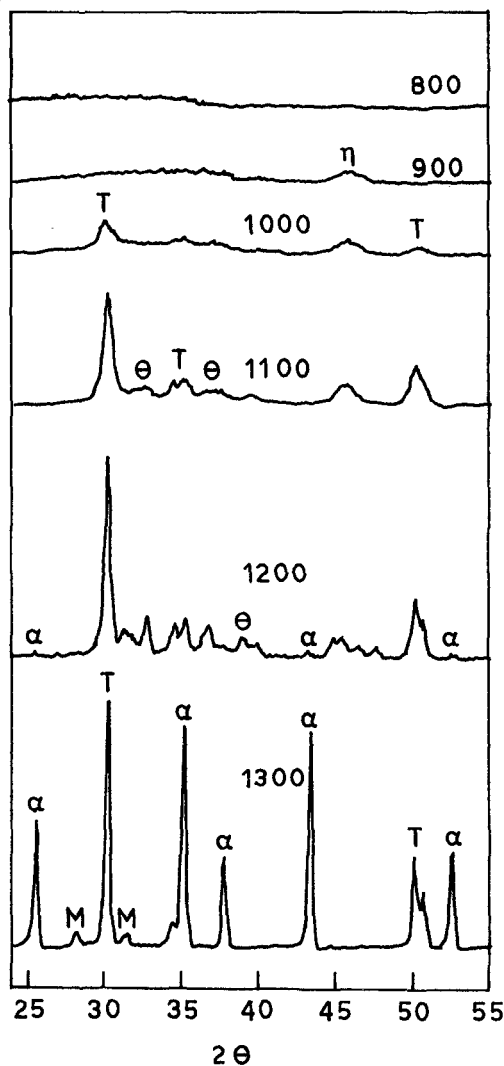


Fig. 1 The XRD patterns of Al_2O_3 -15 wt% ZrO_2 sample calcined at various temperatures for 1h.
 η : η - Al_2O_3 , θ : θ - Al_2O_3 , α : α - Al_2O_3 ,
 T: tetragonal ZrO_2 , M: monoclinic ZrO_2

prepared powders by them already existed in tetragonal form similar to the pure ZrO_2 case in the present study. Hence, in the powders synthesized, whether ZrO_2 exists as tetragonal or noncrystalline form is dependent on the interaction with surrounding alumina components in a fine scale.

Figure 1 shows the XRD patterns of the Al_2O_3 -15 wt% ZrO_2 sample calcined at various temperatures. The sample yields a completely amorphous pattern up to 800°C. An η - Al_2O_3 structure is identified around 900°C. The η - Al_2O_3 completely transforms to α - Al_2O_3 through θ - Al_2O_3 by 1300°C. During the η - θ transformation of Al_2O_3 , tetragonal ZrO_2 precipitates around 1000 to 1100°C. Most of the tetragonal form was conserved even after calcining at 1400°C.

The absence of tetragonal ZrO_2 until η - Al_2O_3 transformation to the θ - Al_2O_3 intermediate suggests that aluminum and zirconium atoms are homogeneously

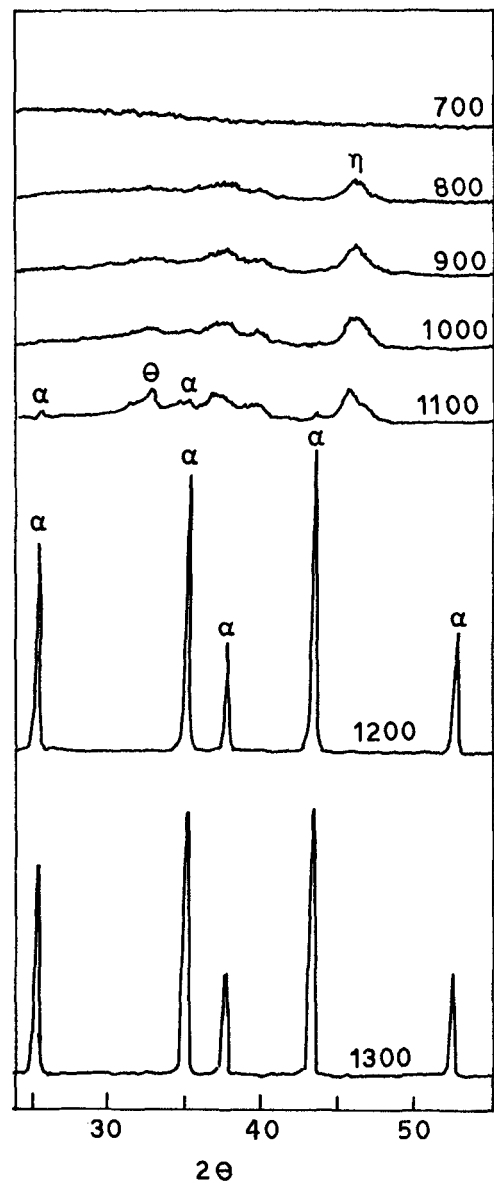


Fig. 2 The XRD patterns of pure Al_2O_3 samples calcined at various temperatures for 1h.
 η : η - Al_2O_3 , θ : θ - Al_2O_3 , α : α - Al_2O_3

mixed on an atomic scale in the as-prepared sample, and zirconium atoms are subsequently incorporated into the defect matrix of η - Al_2O_3 . Similar results were previously reported in Al_2O_3 -10 vol% ZrO_2 system prepared by heating an amorphous precursor Al/Zr copolymerized alkoxide network structure.¹¹ It was described that tetragonal ZrO_2 precipitated during γ - θ transformation of Al_2O_3 . For the present system, a high homogeneity of components in the as-synthesized powders can be expected because of similarities of starting materials of $\text{Al}(\text{NO}_3)_3$ and $\text{ZrO}(\text{NO}_3)_2$ in pyrolysis. They have relatively large solubilities for water and ethanol and relatively lower pyrolysis-temperatures, both of which greatly influence the characteristic of resulting powders.

Figure 2 shows the XRD patterns of pure Al_2O_3 samples calcined at various temperatures. An η -

structure is already detected by 800 °C. The conversion to α -structure is completed by 1200 °C. Thermal decomposition of $\text{Al}(\text{NO}_3)_3$ was studied by several workers. Tsuchida et al.¹² reported that η - Al_2O_3 crystallized from amorphous phase at 860 °C and transformed to α - Al_2O_3 through θ - Al_2O_3 at 1100 °C. It can be seen that the crystallization behavior of the spray pyrolyzed pure- Al_2O_3 sample is similar to the results in their report, although a certain difference in the crystallization temperatures is recognized.

Comparison of the results in Fig. 1 for the samples contained 15 wt% ZrO_2 with those in Fig. 2 for the pure Al_2O_3 samples reveals that the presence of ZrO_2 greatly inhibits the crystallization of Al_2O_3 . Similar effect was reported in Al_2O_3 -10 vol% ZrO_2 system prepared from alkoxides.¹¹

Figure 3 shows the crystallization temperatures of η - and α - Al_2O_3 as a function of ZrO_2 content for the as-prepared powders. The formation temperature of η - Al_2O_3 continuously increases with increasing ZrO_2 content up to around 20 wt% ZrO_2 . The formation temperature of α - Al_2O_3 abruptly increases with increasing ZrO_2 content and already shows the saturation by 5 wt% ZrO_2 . The difference in the crystallization behavior between η - and α - Al_2O_3 can be ascribed to the states of ZrO_2 presented within them. ZrO_2 exists as a noncrystalline phase incorporated within the defect matrix of η - Al_2O_3 , whereas thereafter ZrO_2 crystallizes to tetragonal form before the α - Al_2O_3 formation.

Figure 4 shows the variation of particle structure with calcining for the Al_2O_3 -15 wt% ZrO_2 sample observed using TEM. As-prepared particles are found to be

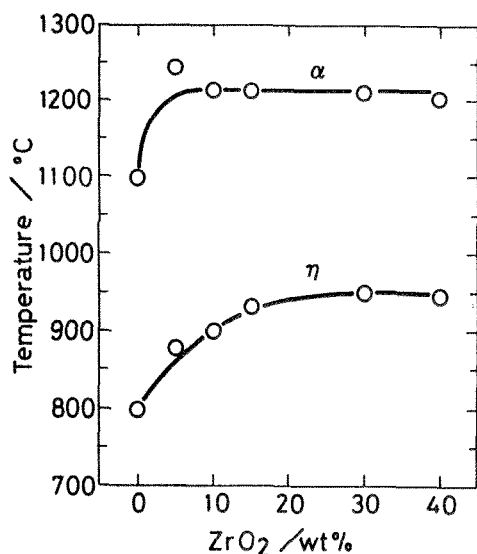


Fig. 3 Crystallization temperatures of η - and α - Al_2O_3 as a function of ZrO_2 content for the spray pyrolyzed samples. The crystallization temperature means the temperature at the extrapolated onset measured on the DTA curves.

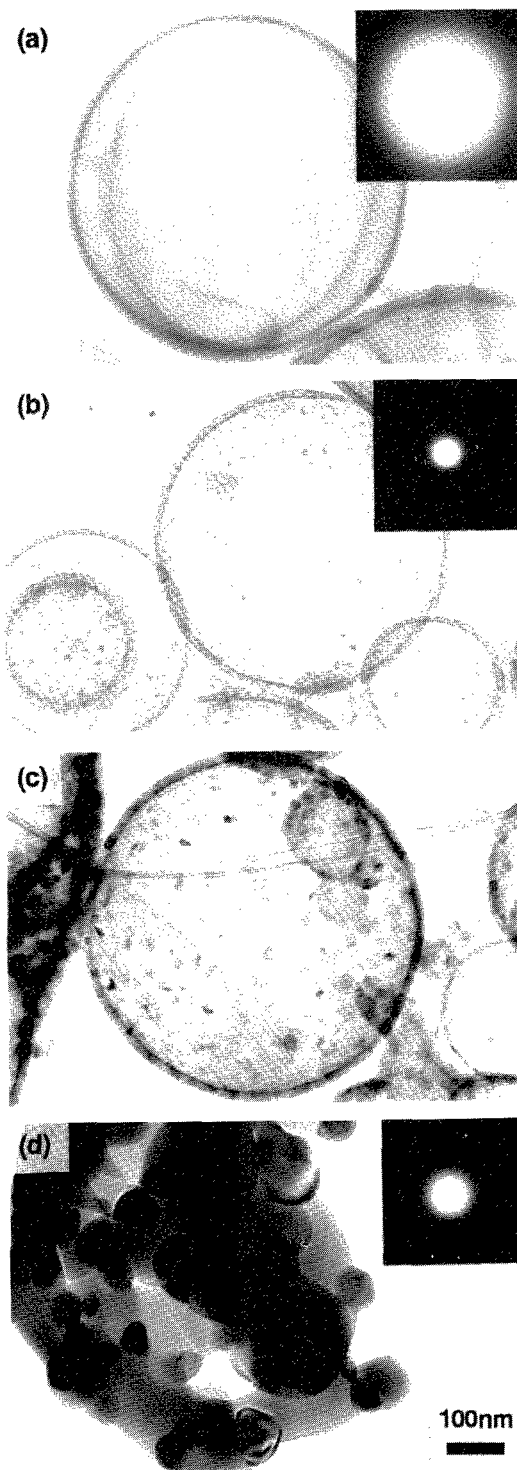


Fig. 4 The TEM photographs and the electron diffraction patterns (right-corner) of Al_2O_3 -15 wt% ZrO_2 samples calcined at various temperatures for 1h. (a) as-prepared, (b) 1100°C, (c) 1200°C, (d) 1300°C

hollow spherical with very thin shell and shows no precipitate. They give the hollow pattern of electron diffraction corresponding to non-crystalline phase as well as the XRD results (Fig. 1). The sample calcined at 1100°C shows very fine precipitates in each particle. These precipitates gradually grow with increasing

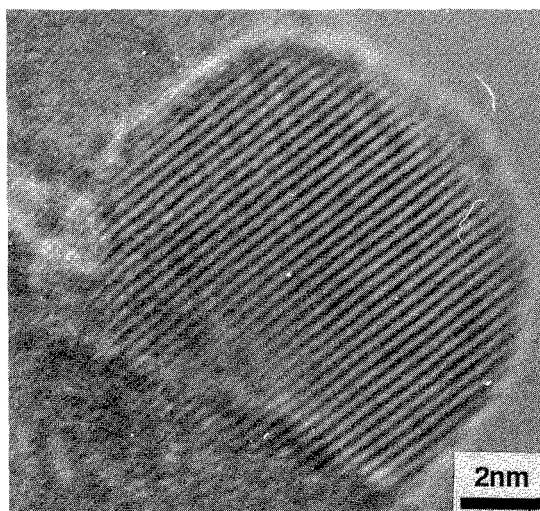


Fig. 5 The lattice image of ZrO_2 grain in the Al_2O_3 -15 wt% ZrO_2 sample calcined at 1100 °C for 1h.

calcining temperature. The sample calcined at 1300°C exhibits deformed and collapsed particle morphology caused by grain growth and partial sintering of the precipitates. Fine dispersed grains with dark contrast and matrix grains with bright contrast are clearly distinguishable. The former grains were analyzed to be ZrO_2 and the latter to be Al_2O_3 by EDX. The ZrO_2 grains are found to be only 40 nm in size and significantly small compared with those in the literature.¹¹ This small grain size is probably attributed to restriction of the grain growth by the unusual particle morphology; that is, it is hollow sphere of very thin film. It should be noted that the ZrO_2 grains are partly incorporated into surrounding Al_2O_3 matrix grains. The structure of the ZrO_2 grains was analyzed in detail by high resolution analysis.

Figure 5 illustrates the lattice image of the ZrO_2 grain in the Al_2O_3 -15 wt% ZrO_2 sample calcined at 1100 °C. The ZrO_2 grain is found to be single crystal 11 nm in size. The lattice image depicts the d-spacing of 0.306 nm corresponding to tetragonal ZrO_2 (111) plane. The similar observation clarified that ZrO_2 grains in the sample (15 wt% ZrO_2) calcined at 1300°C was also single crystal of tetragonal structure. The observed grain size of ZrO_2 was confirmed to agree with the crystallite size measured by XRD.

The existence of the tetragonal ZrO_2 at room temperature has been attributed to a number of factors,¹³⁻¹⁶ including crystallite size, constraint effect of matrix, nucleation difficulties, and so on. The sample (15 wt% ZrO_2) was confirmed to maintain 90% of tetragonal phase even after calcining at 1400 °C by XRD. In this sample, the crystallites of tetragonal phase were conserved to only 50 nm in size, which is accounted as one of the factors for the preservation of tetragonal phase. As mentioned above (Fig. 4), this will be caused by the peculiar structure of particles of synthesized powders. Furthermore, tetragonal ZrO_2 exists as single crystals that were non-contiguously distributed and partly incorporated into matrix Al_2O_3 grains. This naturally leads to the consideration that

the ZrO_2 grains in the samples can be applied the relatively strong compressive stress from the matrix grains against the tetragonal to monoclinic transformation accompanying the large volumetric expansion compared with a sample prepared by the conventional oxide mixing method. It is also supposed that the fine noncontiguous ZrO_2 grains is possibly advantageous for the hindrance of the nucleation of monoclinic ZrO_2 .

4. CONCLUSIONS

Particle structures and crystallization behavior of Al_2O_3 - (0-40 wt%) ZrO_2 powders synthesized by the spray pyrolysis technique have been studied. The results obtained are summarized as follows:

1. As-prepared powders were composed of fine and hollow spherical particles of very thin film showing non-crystalline phase.
2. When the samples were calcined, tetragonal ZrO_2 began to crystallize during η - Al_2O_3 - θ - Al_2O_3 conversion around 1000-1100 °C and transformation to α - Al_2O_3 occurred around 1100-1200 °C.
3. The crystallization of aluminas was markedly inhibited by ZrO_2 contained.
4. The ZrO_2 grains formed existed as very fine single crystals uniformly dispersed and partly incorporated within α - Al_2O_3 grains and conserved the tetragonal form even after calcining at 1400 °C.

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