Formation and Sintering of Zirconia (3 mol% Yttria)—Toughened Alumina Powders Prepared by the Hydrazine Method

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Alumina/3 mol% yttria-doped zirconia composite powders have been prepared by the hydrazine method. As-prepared powders are AlO(OH) gel solid solutions and the mixtures of this and amorphous ZrO₂ below and above 10 mol% ZrO₂, respectively. Formation process leading to α-Al₂O₃-t-ZrO₂ composite powders is examined. Hot isostatic pressing has been performed for 1 h at 1500°C under 196 MPa using the composite powders of α-Al₂O₃ and t-ZrO₂ obtained by heating for 1 h at 1350°C. The resulting dense ZrO₂-toughened Al₂O₃ (ZTA) ceramics with 30 mol% ZrO₂ show excellent mechanical strength (1100 MPa). The grain sizes of α-Al₂O₃ and intergranular ZrO₂ in ZTA decrease with increased ZrO₂ addition. Intragranular ZrO₂ grains are 0.3 μm regardless of the starting composition. Mechanical properties are discussed in connection with relative densities and microstructures.

1 Introduction

To enhance the mechanical properties of Al₂O₃ ceramics, it is well known that dispersed ZrO₂ particles in Al₂O₃ matrix play an important role. The so-called ZrO₂-toughened Al₂O₃ (ZTA) ceramics have many applications in which high wear resistance and mechanical strength are required. The mechanical properties of ZTA depend mainly on the amount of ZrO₂ addition, the size of ZrO₂ grains, and the relative content of t-ZrO₂. Two important mechanisms, i.e., microcrack toughening and stress-induced transformation toughening have been proposed to explain the increased toughness of ZTA. The former and the latter are the major phenomena when the dispersed ZrO₂ particles are monoclinic and tetragonal, respectively. The t- to m-ZrO₂ transformation depends on the critical size which is related to Young’s modulus of the matrix, the shape of ZrO₂ particle, the location of ZrO₂ particle (intergranular or intragranular), and the variety of stabilizers (Y₂O₃, CaO, MgO etc.).

To improve the mechanical properties of ZTA, various approaches, such as mechanical mixing of powders, reactive sintering, hot isostatic pressing, sol-gel synthesis, evaporative decomposition of slurry, and spray-ion-coupled plasma (ICP) technique, have been reported in the literature. However, there are still unsolved problems which need to be investigated: (1) sintering at low temperatures, (2) improvement of homogeneity, and (3) retention of the t-ZrO₂ phase, etc. It has previously been reported that in the system ZrO₂-Al₂O₃ a new powder preparation method using hydrazine monohydrate ((NH₂)₂·H₂O) was developed for the formation and sintering of composite powders up to 50 mol% Al₂O₃. In the present study, AlO(OH) gel solid solutions containing up to 10 mol% ZrO₂ with 3 mol% Y₂O₃ addition were formed by the hydrazine method. The present paper deals with the formation and sintering of 3 mol% Y₂O₃-doped ZTA powders.

2 Experimental Procedure

Six compositions, denoted A through F, were prepared by the hydrazine method. Six compositions, denoted A through F, were prepared by the hydrazine method.

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Table 1 Chemical composition of starting powders and temperatures of crystallization and transformation.

<table>
<thead>
<tr>
<th>Starting powder</th>
<th>Composition (mol%)</th>
<th>Crystallization of $t\cdot\text{ZrO}_2$ ($^\circ\text{C}$)</th>
<th>Transformation of $\theta\cdot\text{ to } \alpha\cdot\text{Al}_2\text{O}_3$ ($^\circ\text{C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>95/5</td>
<td>95/4.85/0.15</td>
<td>1210 - 1285</td>
</tr>
<tr>
<td>B</td>
<td>90/10</td>
<td>90/9.70/0.30</td>
<td>1225 - 1310</td>
</tr>
<tr>
<td>C</td>
<td>85/15</td>
<td>85/14.55/0.45</td>
<td>1245 - 1335</td>
</tr>
<tr>
<td>D</td>
<td>80/20</td>
<td>80/19.40/0.60</td>
<td>1260 - 1355</td>
</tr>
<tr>
<td>E</td>
<td>75/25</td>
<td>75/24.25/0.75</td>
<td>1273 - 1375</td>
</tr>
<tr>
<td>F</td>
<td>70/30</td>
<td>70/29.10/0.90</td>
<td>1290 - 1395</td>
</tr>
</tbody>
</table>

chosen for this study (Table 1). Anhydrous aluminum chloride (AlCl₃, 99.9% pure), anhydrous zirconium chloride (ZrCl₄, 99.9% pure), yttrium chloride (YC₁₂·6H₂O, 99.95% pure), and hydrazine monohydrate ((NH₂)₂·H₂O, 80%) were used as starting materials. The former two and the third were adjusted in concentrations of 0.5 mol/l and 0.1 mol/l aqueous solutions, respectively, by dissolving in distilled water. The mixed aqueous solution (pH=2) was stirred with a magnetic stirrer for 30 min at room temperature, and then hydrazine monohydrate was added dropwise to the mixed solution at 60°C, with stirring, until the resulting suspension reached pH=8. Then, the suspension was heated for 1 h at the same temperature. The products were separated from the suspensions by centrifugation, washed more than ten times in hot water to remove adsorbed hydrazine and chloride ion (tested by adding a silver nitrate solution), and then dried at 120°C under reduced pressure. The average particle size of the starting powders, determined by transmission electron microscopy (TEM), was ~5 nm (Fig. 1).

Differential thermal analysis (DTA) was conducted in air at a heating rate of 10°C/min; $\alpha\cdot\text{Al}_2\text{O}_3$ was used as the reference. The starting powders and specimens, obtained from the DTA runs after cooling, were examined by X-ray diffraction (XRD) using Ni-filtered CuKα radiation. Sintering was performed by hot isostatic pressing (HIP) using argon gas as the pressure-transmitting medium. Before HIP, calcined powders were pressed into pellets at 196 MPa and then isostatically cold-pressed at 392 MPa. The green compacts, covered with boron nitride powders, were sealed in a Pyrex-glass tube under vacuum. HIPing conditions were as follows: (1) heating rate of 400°C/h, (2) increasing pressure rate of ~180 MPa/h above 800°C, and (3) sintering for 1 h at 1500°C under 196 MPa. Bulk densities, after lapping with a diamond powder, were measured by the Archimedes method. Scanning electron microscopy (SEM) was utilized for the microstructural observation.

3 Results and Discussion

3.1 Identification of Starting Powder and Thermal Analysis

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Figure 2 shows the XRD patterns of powders B and E, in comparison with that of pure AlO(OH) gel prepared by the present method. All starting powders showed the patterns of AlO(OH) gel, although the XRD lines decreased in intensity with increased ZrO_2 addition. The DTA curves are shown in Fig. 3. Two successive endothermic peaks below 400°C can be attributed to the dehydration of adsorbed water and hydrated water. Endothermic peaks at 400°C to 550°C resulted from the release of the hydroxy group from AlO(OH) gel. Above 800°C thermal behavior was classified into two groups: (1) powders A and B and (2) powders C through F. The starting powder B showed an exothermic peak at 1225°C to 1310°C. As will be described, the peak, as well as in pure Al_2O_3 at 1140°C to 1210°C, was found to result from the transformation of α- to α-Al_2O_3. On the other hand, for powder E two exothermic peaks resulting from the crystallization of t-ZrO_2 and the transformation described above were observed at 860°C to 960°C and 1275°C to 1375°C, respectively. This results suggest that powders C through F contained amorphous ZrO_2. Now, a mixture in the same composition as with powder B was prepared from each product by the present method. The DTA curve of this sample revealed an exothermic peak (880°C-990°C) resulting from the crystallization of t-ZrO_2. Accordingly, it can be concluded that powders A and B and powders C through F were AlO(OH) gel solid solutions and the mixtures of this and amorphous ZrO_2, respectively. Temperatures of crystallization and transformation changed with increased ZrO_2 addition; the former was shifted at lower temperature and the latter at higher temperature (Table 1).

3.2 Reaction Process

Table 2 shows the phase developments for powders B and E. After dehydration of AlO(OH) gel, both powders became amorphous. For powder B γ-Al_2O_3(ss) crystallized above 650°C and the XRD line intensities increased slowly with increasing...
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...temperature. The t-ZrO₂ phase was formed rapidly above 1050°C with the transformation of γ to α-Al₂O₃. Note that t-ZrO₂ was formed by decomposition of γ-Al₂O₃ solid solution. The specimen heated at 1310°C was a mixture of α-Al₂O₃ and t-ZrO₂. On the other hand, for powder E γ-Al₂O₃(ss) and t-ZrO₂ crystallized above 750°C and at 860° to 960°C, respectively. The latter phase grew rapidly above 1100°C. Composite powder of α-Al₂O₃ and t-ZrO₂ was obtained when heated at 1375°C. Figure 4 shows the intensity of the main characteristic XRD line (111) of t-ZrO₂ formed from powders B and E. The important fact is that the formation from powder E proceeded in two steps: (I) crystallization of free amorphous ZrO₂ and (II) decomposition of γ-Al₂O₃ solid solution. The lattice parameter of γ-Al₂O₃ from each starting powder, as well as in AlO(OH) gel, could not be determined because of its weak and wide XRD lines. From the results of DTA and XRD analysis, the reaction process can be summarized as shown in Fig. 5.

3.3 Sintering

α-Al₂O₃/t-ZrO₂ composite powders were prepared by calcining for 1 h at 1350°C. Figure 6 shows the transmission electron micrograph (TEM) of

![Fig. 4](image-url)  
Fig. 4 Intensity of (111) line for t-ZrO₂ from powders (a)B and (b) E: (I) crystallization of free amorphous ZrO₂ and (II) decomposition of γ-Al₂O₃ solid solution.

![Fig. 5](image-url)  
Fig. 5 Reaction process leading to α-Al₂O₃-t-ZrO₂ composite powder.
the composite powder from powder E; t-ZrO₂ particles of ≈35 nm are finely dispersed in translucent Al₂O₃ particles. The calcined powders were sintered by HIP, as described in the experimental section. Table 3 shows the characteristics of ZTA ceramics. XRD analysis on the fracture surfaces of ZTA showed the mixed phase of α-Al₂O₃ and t-ZrO₂. In the calculation of relative densities, the theoretical densities of α-Al₂O₃ and t-ZrO₂ (containing 3 mol% Y₂O₃) were assumed to be 3.987 and 6.067 Mg/m³, respectively. Relative densities >99% of theoretical were obtained and increased with increased ZrO₂ addition. Sintered ZTA from powder F reached 99.9%.

Figure 7 shows SEM photographs for the fracture surfaces of ZTA. As shown in Table 3, the Al₂O₃ grain size decreased from 3.1 to 1.4 μm with increased ZrO₂ addition. However, it changed little for compositions containing 20 to 30 mol% ZrO₂. Intragranular and intergranular ZrO₂ were observed; the grain size of the former was more than that of the latter. Intragranular ZrO₂ of 0.3 μm in size was observed regardless of the starting composition. On the other hand, the grain size of intergranular ZrO₂ depended on the composition; it decreased in the range of 0.75 to 0.45 μm with increased ZrO₂ addition, in proportion to the decreased grain size of α-Al₂O₃.

3.4 Mechanical Properties

After the sintered ZTA were cut with a diamond saw, they were lapped with a diamond powder (nominal size 1-2 μm). Test bar samples for mechanical measurements were 3 mm high, 3 mm wide, and 20 mm long. The fracture toughness (Klc) measurements were made by the microindentation technique with a 490-N Vickers load. Three-point bending strength was measured with a 16-mm span and a crosshead speed of 0.5 mm/min. Figure 8 shows the Klc and bending strength of ZTA as a function of ZrO₂ addition. The Klc increased linearly 5.1-5.5 MPa·m¹/² with increased ZrO₂ addition. The behavior of Klc agreed with data reported previously. In these types of materials, the t-ZrO₂ particles enhance the toughness by creating the "stress-induced" transformation. Accordingly, it is clear that the increased t-ZrO₂

Table 3. Densities and average grain size of ZTA ceramics.

<table>
<thead>
<tr>
<th>Starting powder</th>
<th>Bulk density (g/cm³)</th>
<th>Relative density (%)</th>
<th>Average grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>α-Al₂O₃</td>
</tr>
<tr>
<td>A</td>
<td>4.06</td>
<td>99.2</td>
<td>3.1</td>
</tr>
<tr>
<td>B</td>
<td>4.13</td>
<td>99.4</td>
<td>2.4</td>
</tr>
<tr>
<td>C</td>
<td>4.23</td>
<td>99.7</td>
<td>1.9</td>
</tr>
<tr>
<td>D</td>
<td>4.32</td>
<td>99.7</td>
<td>1.5</td>
</tr>
<tr>
<td>E</td>
<td>4.41</td>
<td>99.8</td>
<td>1.4</td>
</tr>
<tr>
<td>F</td>
<td>4.51</td>
<td>99.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 6. Transmission electron micrograph of α-Al₂O₃/t-ZrO₂ composite powder from powder E (bar=100 nm).
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Particles as the toughening agent resulted in the increase of $K_{IC}$. The bending strength of ZTA increased slowly up to 15 mol% $\text{ZrO}_2$ and then rapidly between 15 and 25 mol% $\text{ZrO}_2$. Finally, the maximum of 1100 MPa was obtained with 30 mol% $\text{ZrO}_2$. The results must be explained in terms of the increased relative density and the decreased grains of $\alpha$-$\text{Al}_2\text{O}_3$ and intergranular $\text{ZrO}_2$. Lange$^{18,20}$ fabricated $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite ceramics consisting of nearly theoretical density in the composition of up to 30 vol% (35.2 mol%) $\text{ZrO}_2$ with 2 mol% $\text{Y}_2\text{O}_3$ and in 30 vol% $\text{ZrO}_2$ with 3 mol% $\text{Y}_2\text{O}_3$ using submicrometer-sized powders prepared by ball-milling. Sintering techniques were hot-pressing ($1600°C/2 \text{ h}$)$^{18}$ and post-HIP ($1500°C/200 \text{ MPa}/1 \text{ h}$)$^{20}$ For this earlier work,$^{18}$ the strength of ZTA increased linearly with increased $\text{ZrO}_2$ addition. The maximum value was 869 MPa in the ZTA fabricated from the 70 $\text{Al}_2\text{O}_3$/30 $\text{ZrO}_2$ (plus 3 mol% $\text{Y}_2\text{O}_3$) vol% powder. Becher$^{19}$ prepared the composite powder with the same composition as described in Ref.20 by a sol-gel technique and reported that the strength of the ZTA fabricated by vacuum hot-pressing ($1425°-1550°C$) was 740 MPa. Thus, the ZTA ceramics from powders E and F in the present study were found to show excellent mechanical strength.

4 Conclusions

In the $\text{Al}_2\text{O}_3$-rich region of the system $\text{ZrO}_2$ -$\text{Al}_2\text{O}_3$, a new method for preparing $\text{Al}_2\text{O}_3$ / 3 mol% $\text{Y}_2\text{O}_3$-doped $\text{ZrO}_2$ composite powders from $\text{AlCl}_3$, $\text{ZrCl}_4$, and $\text{YCl}_3$ using hydrazine monohydrate has been developed. As-prepared powders are $\text{AlO(OH)}$ gel solid solutions and the mixtures of this and amorphous $\text{ZrO}_2$
below and above 10 mol% ZrO₂, respectively. Formation process leading to α-Al₂O₃/t-ZrO₂ composite powders is shown in Fig. 5. Sintering has been preformed for 1 h at 1500°C and 196 MPa by hot isostatic pressing. The resulting dense ZrO₂-toughened Al₂O₃ (ZTA) ceramics (>99% of theoretical) with homogeneous-dispersed ZrO₂ particles show excellent mechanical strength.

References