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

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Received June 13, 1994

Alumina/3 mol% yttria-doped zirconia composite powders have been prepared by the hydrazine method. As-prepared powders are $\text{AlO}(\text{OH})$ gel solid solutions and the mixtures of this and amorphous ZrO_2 below and above 10 mol% ZrO_2 , respectively. Formation process leading to α - Al_2O_3 - t - ZrO_2 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 - Al_2O_3 and t - ZrO_2 obtained by heating for 1 h at 1350°C. The resulting dense ZrO_2 -toughened Al_2O_3 (ZTA) ceramics with 30 mol% ZrO_2 show excellent mechanical strength (1100 MPa). The grain sizes of α - Al_2O_3 and intergranular ZrO_2 in ZTA decrease with increased ZrO_2 addition. Intragranular ZrO_2 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 Al_2O_3 ceramics, it is well known that dispersed ZrO_2 particles in Al_2O_3 matrix play an important role. The so-called ZrO_2 -toughened Al_2O_3 (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 ZrO_2 addition, the size of ZrO_2 grains, and the relative content of t - ZrO_2 . Two important mechanisms, i.e., microcrack toughening^{1,2} and stress-induced transformation toughening^{3,4} have been proposed to explain the increased toughness of ZTA. The former and the latter are the major phenomena when the dispersed ZrO_2 particles are monoclinic and tetragonal, respectively. The t - to m - ZrO_2 transformation depends on the critical size which is related to Young's modulus of the matrix, the shape of ZrO_2 particle, the location of ZrO_2 particle (intergranular or intragranular), and the variety of stabilizers (Y_2O_3 , CaO , MgO etc.).⁵

To improve the mechanical properties of ZTA,

various approaches, such as mechanical mixing of powders,⁶ reactive sintering,⁶ hot isostatic pressing,⁷ sol-gel synthesis,⁸ evaporative decomposition of slurry,⁹ and spray-ion-coupled plasma (ICP) technique,¹⁰ 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 - ZrO_2 phase, etc.^{11,12} It has previously been reported that in the system ZrO_2 - Al_2O_3 a new powder preparation method using hydrazine monohydrate ($(\text{NH}_2)_2\text{H}_2\text{O}$) was developed for the formation and sintering of composite powders up to 50 mol% Al_2O_3 .^{13,14} In the present study, $\text{AlO}(\text{OH})$ gel solid solutions containing up to 10 mol% ZrO_2 with 3 mol% Y_2O_3 addition were formed by the hydrazine method. The present paper deals with the formation and sintering of 3 mol% Y_2O_3 -doped ZTA powders.

2 Experimental Procedure

Six compositions, denoted A through F, were

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

Starting powder	Composition (mol%)		Crystallization of t -ZrO ₂ (°C)	Transformation of θ - to α -Al ₂ O ₃ (°C)
	Al ₂ O ₃ /ZrO ₂ (3mol%Y ₂ O ₃)	Al ₂ O ₃ /ZrO ₂ /Y ₂ O ₃		
A	95 / 5	95 / 4.85 / 0.15	—	1210 - 1285
B	90 / 10	90 / 9.70 / 0.30	—	1225 - 1310
C	85 / 15	85 / 14.55 / 0.45	880 - 980	1245 - 1335
D	80 / 20	80 / 19.40 / 0.60	870 - 970	1260 - 1355
E	75 / 25	75 / 24.25 / 0.75	860 - 960	1275 - 1375
F	70 / 30	70 / 29.10 / 0.90	850 - 950	1290 - 1395

chosen for this study (Table 1). Anhydrous aluminum chloride (AlCl₃, 99.9% pure), anhydrous zirconium chloride (ZrCl₄, 99.9% pure), yttrium chloride (YCl₃·6H₂O, 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; α -Al₂O₃ 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 CuK α 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

Fig. 1 Transmission electron micrograph of powder E (bar=20 nm).

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

Fig. 2 X-ray diffraction patterns for powders (a) B, (b) E, and (c) AlO(OH) gel.

Fig. 3 DTA curves for powders (a) B, (b) E, and (c) AlO(OH) gel.

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 ZrO₂ addition. The DTA curves are shown in Fig. 3. Two successive endothermic peaks below 400°C can be

attributed to the dehydration of absorbed water and hydrated water. Endothermic peaks at 400° to 550°C resulted from the release of the hydroxyl 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° to 1310°C. As will be described, the peak, as well as in pure Al₂O₃ at 1140° to 1210°C, was found to result from the transformation of θ - to α -Al₂O₃. On the other hand, for powder E two exothermic peaks resulting from the crystallization of *t*-ZrO₂ and the transformation described above were observed at 860° to 960°C and 1275° to 1375°C, respectively. This results suggest that powders C through F contained amorphous ZrO₂. 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°-990°C) resulting from the crystallization of *t*-ZrO₂. 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 ZrO₂, respectively. Temperatures of crystallization and transformation changed with increased ZrO₂ 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 -Al₂O₃(ss) crystallized above 650°C and the XRD line intensities increased slowly with increasing

Table 2 Phases identified for specimens quenched after heating to various temperatures .

Starting Powder	Phase identified										
	550° - 650°C	650° - 750°C	750° - 860°C	860° - 1050°C	1050° - 1100°C	1100° - 1225°C	1225° - 1275°C	1275° - 1310°C	1310° - 1375°C	1375° - 1400°C	
B	Amorphous	γ -Al ₂ O ₃ (ss)	γ -Al ₂ O ₃ (ss)	γ -Al ₂ O ₃ (ss)	γ -Al ₂ O ₃ (ss) θ -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	γ -Al ₂ O ₃ (ss) θ -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	γ -Al ₂ O ₃ (ss) θ -Al ₂ O ₃ α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	θ -Al ₂ O ₃ α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	
E	Amorphous	Amorphous	γ -Al ₂ O ₃ (ss)	γ -Al ₂ O ₃ (ss) <i>t</i> -ZrO ₂ (ss)	γ -Al ₂ O ₃ (ss) <i>t</i> -ZrO ₂ (ss)	γ -Al ₂ O ₃ (ss) θ -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	γ -Al ₂ O ₃ (ss) θ -Al ₂ O ₃ α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	θ -Al ₂ O ₃ α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	θ -Al ₂ O ₃ α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	α -Al ₂ O ₃ <i>t</i> -ZrO ₂ (ss)	

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.

temperature. The t -ZrO₂ phase was formed rapidly above 1050°C with the transformation of γ - to θ -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

(a) Starting powder B

(b) Starting powder E

Fig. 5 Reaction process leading to α -Al₂O₃- t -ZrO₂ composite powder.

Fig. 6 Transmission electron micrograph of $\alpha\text{-Al}_2\text{O}_3/t\text{-ZrO}_2$ composite powder from powder E (bar=100 nm).

the composite powder from powder E; $t\text{-ZrO}_2$ particles of ≈ 35 nm are finely dispersed in translucent Al_2O_3 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 $\alpha\text{-Al}_2\text{O}_3$ and $t\text{-ZrO}_2$. In the calculation of relative densities, the theoretical densities of $\alpha\text{-Al}_2\text{O}_3$ and $t\text{-ZrO}_2$ (containing 3 mol% Y_2O_3) were assumed to be 3.987 and 6.067 Mg/m^3 , respectively.¹⁵ Relative densities >99% of theoretical were obtained and increased with increased ZrO_2 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 Al_2O_3 grain size decreased from 3.1 to 1.4 μm with increased ZrO_2 addition. However, it changed little for compositions containing 20 to 30 mol% ZrO_2 . Intragranular and intergranular ZrO_2 were observed; the grain size of the former was more than that of the latter. Intragranular ZrO_2 of 0.3 μm in size was observed regardless of the starting composition. On the other hand, the grain size of intergranular ZrO_2 depended on the composition; it decreased in the range of 0.75 to 0.45 μm with increased ZrO_2 addition, in proportion to the decreased grain size of $\alpha\text{-Al}_2\text{O}_3$.

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 (K_{IC}) measurements were made by the microindentation technique^{16,17} 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 K_{IC} and bending strength of ZTA as a function of ZrO_2 addition. The K_{IC} increased linearly 5.1-5.5 $\text{MPa}\cdot\text{m}^{1/2}$ with increased ZrO_2 addition. The behavior of K_{IC} agreed with data reported previously.^{18,19} In these types of materials, the $t\text{-ZrO}_2$ particles enhance the toughness by creating the "stress-induced" transformation.^{3,4} Accordingly, it is clear that the increased $t\text{-ZrO}_2$

Table 3 Densities and average grain size of ZTA ceramics.

Starting powder	Bulk density (g/cm^3)	Relative density (%)	Average grain size (μm)		
			Intragranular Intergranular		
			$\alpha\text{-Al}_2\text{O}_3$	$t\text{-ZrO}_2$	$t\text{-ZrO}_2$
A	4.06	99.2	3.1	0.30	0.75
B	4.13	99.4	2.4	0.30	0.56
C	4.23	99.7	1.9	0.30	0.53
D	4.32	99.7	1.5	0.30	0.50
E	4.41	99.8	1.4	0.30	0.47
F	4.51	99.9	1.4	0.30	0.45

Fig. 7 Scanning electron micrographs for fracture surface of ZTA ceramics from powders (a) A, (b) C, and (c) E (bar=5 μm).

particles as the toughening agent resulted in the increase of K_{IC} . The bending strength of ZTA increased slowly up to 15 mol% ZrO_2 and then rapidly between 15 and 25 mol% ZrO_2 . Finally, the maximum of 1100 MPa was obtained with 30 mol% 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 ZrO_2 . Lange^{18,20} fabricated

Fig. 8 Fracture toughness and bending strength of ZTA ceramics.

$\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite ceramics consisting of nearly theoretical density in the composition of up to 30 vol% (35.2 mol%) ZrO_2 with 2 mol% Y_2O_3 and in 30 vol% ZrO_2 with 3 mol% Y_2O_3 using submicrometer-sized powders prepared by ball-milling. Sintering techniques were hot-pressing (1600°C/2 h)¹⁸ and post-HIP (1500°C/200 MPa/1 h).²⁰ For this earlier work,¹⁸ the strength of ZTA increased linearly with increased ZrO_2 addition. The maximum value was 869 MPa in the ZTA fabricated from the 70 Al_2O_3 /30 ZrO_2 (plus 3 mol% Y_2O_3) vol% powder. Becher¹⁹ 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 Al_2O_3 -rich region of the system ZrO_2 - Al_2O_3 , a new method for preparing Al_2O_3 / 3 mol% Y_2O_3 -doped ZrO_2 composite powders from AlCl_3 , ZrCl_4 , and YCl_3 using hydrazine monohydrate has been developed. As-prepared powders are $\text{AlO}(\text{OH})$ gel solid solutions and the mixtures of this and amorphous ZrO_2

below and above 10 mol% ZrO_2 , respectively. Formation process leading to $\alpha\text{-Al}_2\text{O}_3/\text{t-ZrO}_2$ 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 ZrO_2 -toughened Al_2O_3 (ZTA) ceramics (>99% of theoretical) with homogeneous-dispersed ZrO_2 particles show excellent mechanical strength.

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