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Preparation and characterization of an Al₂O₃–ZrO₂ nanocomposite, Part I: Powder synthesis and transformation behavior during fracture

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Abstract

An alumina–zirconia composite containing 5 mol% zirconia was prepared by following a wet interaction process in aqueous medium via the sol–gel route. The formed hydrogel which was aged for proper growth and orientation at room temperature, was then dried at a low temperature to minimize agglomeration. The sol–gel derived precursor powder was properly characterized through determination of surface area, particle size and thermal analysis. The sintering behavior was studied by compacting the nano-powder through cold isostatic pressing where maximum densification of 98.4% was achieved at 1550 °C. During Vickers indentation using a 5 kg load, cracks were propagating around the grain boundaries and fractured the ZrO_2 particles, which was associated with *t*- ZrO_2 to *m*- ZrO_2 transformation. Sintering was studied in the absence of a mineraliser.

Keywords: Sol-gel processing; A. Nano-structures; B. Mechanical properties; D. Fractography

1. Introduction

Zirconia-toughened alumina (ZTA) ceramics have received significant scientific and technological attention during the last two decades for use in cutting tools, dies or prosthesis components due to their excellent room temperature strength, toughness and wear resistance [1]. The fine grain size and uniform microstructure satisfy these requirements; moreover, toughness can be improved many folds due to the presence of a possible 100% transformable tetragonal phase within the alumina matrix. The retention of t-ZrO₂ has to be controlled carefully until the composite is used for service. It has been recognized that the magnitude of toughening is complexly dependent on the microstructure of the alumina–zirconia composite (i.e., volume fraction, size, shape, location and size distribution of ZrO_2) [2,3]. Homogeneous as well as fine dispersions of ZrO_2 particles in the alumina matrix can be obtained by chemical mixing of the constituents in the solution. Hence, the sol-gel processing is used in the present work to prepare alumina-zirconia composite powders.

Sol-gel processing technology has been developed for the fabrication of a high quality ceramic-based composite. For complex oxides, it achieves ultra-homogeneous mixing of the several components on a molecular scale, reduces sintering temperature and hence develops a fine-grained microstructure. Thus, the liquid precursor technology offers processing advantages and gives flexibility in tailoring the composite chemistry to obtain the desired properties [4–6]. Moreover, the processing conditions, composition, retention of the *t*-phase of zirconia and the calcination temperature strongly influence the morphology of the powder and sintering behavior [6–9]. The arguments and observations responsible for such modifications are changeable with the phase composition, crystallinity,

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crystallite size and pore morphology, specific surface area and subsequent shrinkage. Several methods of preparing alumina–zirconia powders and composites have been reported elsewhere [4–9].

To our knowledge, martensitic transformation behavior of t-ZrO₂ phase due to Vickers indentation fracture has not been reported elsewhere for undoped 5% zirconia-dispersed alumina composites. Although, the crack growth mechanism through the double-torsion method is reported [10]. Casellas et al. reported that yttria stabilized ZrO₂ can enhance the fracture toughness with respect to the alumina matrix in Vickers indentation [11]. The aim of this research is to obtain undoped alumina–zirconia ultra-fine composites with a homogeneous microstructure of fine intergranular zirconia particles located in alumina triple points by using a sol–gel route and to study the transformation behavior at room temperature during fracture.

2. Experimental

2.1. Powder processing and consolidation

Aqueous solutions of Al(NO₃)₃·9H₂0 (E-Mark, India) and ZrOCl₂·8H₂O (E-Mark, India) were used as the starting materials. The mixed hydrogel was obtained by adding 1:1 NH₃ solution to the mixed aqueous solution maintained at 25 °C with continuous stirring. The viscosity of the batch gradually increased and finally set to an enblock gel at pH 8.7. The gels were then aged at room temperature for 48 h. After aging, the gel was repeatedly washed with boiled distilled water to remove extraneous impurities and filtered. The filtered cake was dried at 40 °C for 48 h. The dried gel was calcined in a muffle furnace at 900 °C for 4 h in air and wet milled in acetone media in a high-density polythene bottle for 24 h using high purity zirconia balls. The powder was again dried at 40 °C. The detailed process flow chart of powder preparation is shown in Fig. 1. The A1₂O₃–ZrO₂ powder was prepared with a composition of 95A1₂0₃-5ZrO₂ (mol%). The mixed powder was consolidated by uniaxial pressing in high carbon steel mould at 5 MPa without any extra binder. Five percent uncalcined powder was used as binder. The pellets were consolidated by cold isostatic pressing at 150 MPa for 2 min. Specimens were sintered in a muffle furnace at different temperatures ranging from 1450 °C to 1600 °C with an interval of 50 °C at different time schedules.

2.2. Powder characterization

Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out in an (STA 409C) system in air at the heating rate of 10 °C/min with the Al₂O₃–ZrO₂ dried gel. For phase analysis of the dried gel and calcined powder, X-ray data were collected using a fully automated Philips X-pert system (PHILIPS PW1830) with Cu-K_{α} radiation. The voltage and the current were set at 40 kV and 20 mA, respectively, with the copper target, with a step



Fig. 1. The typical flow chart of the processing of Al_2O_3 – ZrO_2 composite nano-powder.

size of 0.02° (2 θ) and a count time of 1 s per step. The crystallite size of the synthesized powder was determined from the X-ray line broadening using Sherrer's equation as follows:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where *D* is the crystallite size, λ is wavelength of the radiation, θ is the Bragg's angle and β is the full width at half maximum. Line broadening due to the equipment was substracted from the peak width before calculating the crystallite size using the following formula:

$$B^2 = B_{\text{meas}}^2 - B_{\text{Equip}}^2 \tag{2}$$

Then the as-synthesized Al_2O_3 – ZrO_2 powders were characterized for specific average surface area using a surface area analyzer (Coulter SA 3100 BET) and TEM (JEM 2000 FX) was used for the determination of exact particle size. An ultrasonic equipment (Sidilu Ultrasonics, India) was used in order to obtain well dispersed and agglomerate-free suspensions. The particle size distribution analysis (volume percent) of the suspension was carried out in a computercontrolled particle size analyzer (Malvern, Mastersizer 2000, UK) via a software program. Sintering mechanism and kinetics were studied in a dilatometer (Netzsch DIL 402C) on the pressed specimen (\emptyset 12 mm, length 3 mm) up to 1550 °C for 4 h. The bulk density of the sintered specimen was measured by Archimedes' method.

2.3. Microstructure and mechanical characterization

The microhardness of the sintered specimen (1550 °C for 4 h) was determined applying a Vickers indenter and calculated as $H = P/2d^2$, d being the half-diagonal indentation impression and P the indentation load (4.9 N). $K_{\rm Ic}$ was measured by the indentation method, where the length of cracks emanating from the Vickers indentation corners. $K_{\rm Ic}$ was calculated using the expression proposed by Anstis et al. [12] :

$$K_{\rm Ic} = 0.016 \left[\frac{E}{H}\right]^{0.5} \frac{P}{C^{3/2}}$$
(3)

where E is Young's modulus and C is the crack length.

The reported values were the average of data obtained from five indentation tests. The elastic modulus (*E*) was measured using an ultrasonic tester employing the pulseecho technique. A continuous 5 kg Vickers indentation was applied on the polished surface along the diameter and broke the sample along the indentation. XRD was performed on both the polished and fractured surfaces to determine the phase composition of the sintered materials. The fraction of monoclinic ZrO_2 in the polished and fractured surface was calculated using the following equation [13]:

$$X_{\rm m} = \frac{I_{\rm m}(111) + I_{\rm m}(11\underline{1})}{I_{\rm m}(111) + I_{\rm m}(11\underline{1}) + I_{\rm t}(111)} \tag{4}$$

Furthermore, specimens sintered in the dilatometer were polished and thermally etched (1500 °C/30 min) and fractographs studied by SEM (JEOL-JSM840) and EPMA (EPMA JEOL-JXA8600) of both polished and fractured surfaces.

3. Results and discussion

3.1. Powder characterization

The DTA and TG analyses of dried gel are shown in Fig. 2. The endothermic peak at 110 °C is due to the expulsion of physically bonded water, whereas, the exothermic peak at 280 °C is attributed to the crystallization of t-ZrO₂ [14]. The XRD analysis of calcined powder $(300 \degree C \text{ for } 8 \text{ h})$ also confirms the presence of the *t*-ZrO₂ phase. Again, the endothermic peak at 310 °C corresponds to the transformation of Al(OH)₃ and γ -AlOOH into γ -alumina. The crystallization temperature reduces because of the very fine particle size [15]. The XRD analysis and the determination of particle size also confirm the presence of a very small particle size (Fig. 3). The formation of α-Al₂O₃ completes at 1210 °C with a small exothermic peak [16]. The phase transformation from γ -AlOOH to α -Al₂O₃ follows the following path as reported by earlier researchers [17].

$$\gamma \text{-AlOOH} \stackrel{400 \,^{\circ}\text{C}}{\longrightarrow} \gamma \text{-Al}_2\text{O}_3 \stackrel{800 \,^{\circ}\text{C}}{\longrightarrow} \delta \text{-Al}_2\text{O}_3 \stackrel{1000 \,^{\circ}\text{C}}{\longrightarrow} \theta \text{-Al}_2\text{O}_3$$
$$\stackrel{1200 \,^{\circ}\text{C}}{\longrightarrow} \alpha \text{-Al}_2\text{O}_3$$
(5)

The reduction of specific volume to the extent of 24% is observed in the phase transformation of boehmite (0.332 cc/g) to α -Al₂O₃ (0.251 cc/g), which assists the structure of meso-porous particles. It is expected that finer particles will reduce the transformation temperature due to a very high specific surface area. Therefore, powders are calcined at 900 °C for 4 h to avoid the coarsening effect. The XRD patterns of the calcined powder represents the boehmite and Al(OH)₃ are transformed into δ -Al₂O₃ and θ -Al₂O₃, and amorphous ZrO₂ formed during gel formation is transformed into *m*-ZrO₂ and *t*-ZrO₂ (Fig. 2 and Table 1). The broadening of peaks in XRD patterns con-



Fig. 2. TG/DTA plot for the Al₂O₃-ZrO₂ precursor powders in air.



Fig. 3. Room temperature X-ray diffraction plot for the dried gel at $40 \text{ }^{\circ}\text{C}/48 \text{ h}$ (a) Al₂O₃–ZrO₂ nano-powders calcined at 900 $^{\circ}\text{C}$ for 4 h (b).

Table 1

Different phase contents of dried gel, calcined powder, polished surface and fractured surface of the Al_2O_3-5 mol%ZrO₂ composite

Different phase of ZTA composite	Phase content
Dried gel (40 °C/48 h)	AlO(OH), Al(OH) ₃
Calcined powder (900 °C/4 h)	δ -Al ₂ O ₃ , θ -Al ₂ O ₃ , <i>t</i> -ZrO ₂ , <i>m</i> -ZrO ₂
Polished surface	α-Al ₂ O ₃ , t-ZrO ₂ (100%)
Fractured surface	α-Al ₂ O ₃ , t-ZrO ₂ (~85%), m-ZrO ₂ (~15%)

firmed that the average crystallite size is small. The crystallite size of the dried gel is calculated using Scherrer's equation and the size varies between 5 nm and 20 nm. The crystallite size of the calcined powder is in the range of 25-170 nm.

A transmission electron microscope (TEM) is used to analyze the particle size and morphology of the nano-pow-



Fig. 4. TEM photograph of $5\,mol\% ZrO_2$ doped Al_2O_3 nano-powder. Precursor powders were calcined at 900 °C for 4 h.

Table 2	
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Particle size analysis for the sol–gel synthesized Al_2O_3 –5 mol%ZrO₂ powders by laser diffraction particle size analysis

%<	D_{10}	D_{25}	D_{50}	D_{75}	D_{90}	Mean
Volume statistics size (μm)	0.027	0.045	0.11	0.175	0.229	0.127

der particles. Fig. 4 shows the bright field micrograph of ZTA powders synthesized using $95Al_2O_3-5ZrO_2$ (mol%) and calcined at 900 °C for 4 h. Most of the particles are in the range of 20-200 nm. The phenomenon of high meso-porosity within particles can also be observed in this TEM picture and most of the particles are spherical in nature. TEM studies of powders calcined at 900 °C temperature show agglomeration in the powder. The specific surface area of the final powders is determined by the BET surface area analysis and is calculated as about \sim 130 m²/g. The cumulative statistics of the particle size distribution, as shown in Table 2 for as produced powders, are represented as D₁₀, D₂₅, D₅₀, D₇₅ and D₉₀ corresponding to the particle sizes below 10%, 25%, 50%, 75% and 90% of the total volume of particles analyzed, respectively. The ultra-fine particles as fine as 27 nm are synthesized by the present coprecipitation route.

3.2. Densification and phase analysis

It is noticed during uniaxial pressing (at 5 MPa) that high surface area powders have significant effects on green density. The low green density (1.63 g/cc) is due to the result of the high meso-porosity in synthesized powders (Fig. 4), which are also difficult to compact. An average green density of 1.85 g/cc is achieved after cold isostatic pressing of green compacts at 150 MPa. Densification studies are carried out in both the muffle furnace as well as a dilatometer in atmospheric conditions. The variation of



Fig. 5. Relative density vs sintering temperature of the Al_2O_3 -5 mol%ZrO₂ composite.

 Table 3

 Densification of ZTA pellets after sintering at different conditions

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Sintering temperature (°C)	1450	1500			1550			1600	
Soaking time (h)	2	2	3	4	2	3	4	2	3
Relative density (%)	72.5	77.2	81.1	86.9	88.3	92.4	98.4	97.6	99.2

bulk density after sintering at different temperatures with varying soaking times is shown in Fig. 5. The highest bulk density is attained for the composite powder sintered at 1600 °C for 3 h. Table 3 also summarizes the sinter densities of ZTA pellets sintered for 2 h at 1450, 1500, 1550 and 1600 °C. The transformation of boehmite to α -Al₂O₃ is associated with 24 vol% porosity formations and it is extremely difficult to remove the residual pores trapped within α -alumina grains during the final stage of conventional sintering [18]. This factor is even severe for the low bulk density for the powder calcined at lower temperatures. It can also be noticed that 97.6% densification was achieved at 1600 °C for 2 h due to the higher sintering ability of these ultra-fine powder particles at high temperatures.

The relative densities of the pellets after sintering at 1500, 1550 and 1600 °C for 3 h, the relative densities were 81%, 92% and 99%, respectively, as shown in Table 3. A significant grain growth is observed during sintering at 1600 °C for 3 h using nano-powders, which is an inherent drawback of conventional sintering. Non-conventional heating like microwave sintering, spark plasma sintering etc. may produce materials with near full densities. Sintering was also carried out in a dilatometer up to 1550 °C for 4 h with an initial heating rate of 10 °C/min up to 1000 °C and at the reduced rate of 5 °C/min thereafter. Fig. 6 represents a linear shrinkage of 18% mainly due to the transformation of monoclinic to tetragonal zirconia. Beyond 1200 °C the slope changes due to completion of α -Al₂O₃.

2 0 -2 -4 -6 ⁻⁶ ⁻⁸ ⁻⁸ 10 -12 -14 -16 -18 400 600 800 1000 1200 1400 Temperature (°C)

Fig. 6. Shrinkage of the 95Al₂O₃-5 mol%ZrO₂ composite at 1550 °C/4 h.

Pores are also eliminated with an achievement of 98.4% of the theoretical density of that particular composition. The rate of shrinkage is highest within the *m*-ZrO₂ to *t*-ZrO₂ transformation temperature i.e., $970 \degree C-1170 \degree C$. The behavior of the shrinkage curve quite resembles the nanocrystalline ZrO₂ rather than coarse-grained ZrO₂ [19]. The present results show the better sinterability with the nano-sized starting powders mainly due to the high surface area of ultra-fine particles. The density of the pellets sintered at 1500 °C for 4 h is lower than those of 1600 °C for 3 h; however, grain sizes of the former are smaller. Hence, the detail phase analysis, microstructure and mechanical properties (hardness and fracture toughness) are carried out and reported for the pellet sintered at 1550 °C for 4 h.

The XRD analysis of the polished surface shows that almost 100% of the *t*-phase is retained without using any dopant (Fig. 7a). The simultaneous sintering and phase transformations may provide a better opportunity for low temperature sintering of the alumina–zirconia composite than the more conventional approach on the basis of alumina.

3.3. Microstructure and mechanical properties

Fig. 8a illustrates the scanning electron microstructure of the polished and thermally etched surface of the sintered (1550 °C for 4 h) Al_2O_3 –ZrO₂ composite. Thermal etching is carried out at 1500 °C for 30 min. The SEM image reveals that ZrO₂ particles are present as either intergranular or intragranular in the Al_2O_3 matrix when coprecipitated gels are aged for 48 h. However, the presence of intragranular particles is less compared to intergranular particles. This intergranular grain dominates the transformation mechanism. The average grain size of alumina varies from 0.8 µm to 4 µm and fairly homogeneous in the entire matrix. Zirconia particles are smaller in size



Fig. 7. Room temperature X-ray diffraction plot for $Al_2O_3\text{--}ZrO_2$ compacts sintered at 1550 $^\circ C$ for 4 h.



Fig. 8. Scanning back-scattered electron microscopy images showing the microstructure of polished and thermal etched surface (a) and fracture surface (b) of the Al_2O_3 -5 mol%ZrO₂ composite (sintered at 1550 °C for 4 h). The phases with darker and white and contrasts indicate Al_2O_3 and ZrO₂, respectively. The arrow indicates the pore of the sintered body.

(100–300 nm) and are isolated at grain boundaries between larger alumina grains. The X-ray diffraction confirms these ZrO_2 particles mainly as the tetragonal phase (Fig. 7a). The dimensions of few large zirconia grains are comparable to alumina grains and the absence of zirconia agglomerates indicates a homogeneous relative distribution of both phases in the composite [20]. The X-ray mapping (EPMA analysis) of polished and thermally etched surface shows the presence of different elements (Al and Zr) within the matrix as illustrated in Fig. 9. An uniform distribution of Al and Zr elements are clearly observed in the composite and resembles their relative amounts. This homogeneous distribution is due to homogeneous particle size distribution of the starting powders (see Table 2).

The principal merit of the microstructure observed in the alumina-zirconia composites obtained by the sol-gel route is the adequate relative grain size ratio and phase distribution between the both phases, allowing zirconia particles to be present mostly at grain boundaries without agglomerates. It has been reported that the phase transformation θ to α -A1₂0₃ follows the nucleation and growth process [21]. During the grain growth, a considerable amount of fine pores are redistributed throughout the alumina matrix. Simultaneously, ZrO₂ particles are trapped within the α -Al₂O₃ grains grown from the fine-grained matrix. The microstructure of ZTA sintered bodies (Fig. 8) in this study also confirms the same. The presence of small ZrO₂ particles in the starting materials hinders considerable grain growth of Al₂O₃.

Different experimental techniques like XRD and SEM are used to discern the operative toughening mechanisms. The contribution of stress-induced phase transformation is evaluated by XRD, which is assessed in terms of the amount of monoclinic phase. The phase analysis of the fractured surface reveals the transformation of ~15% *m*-ZrO₂ from *t*-ZrO₂ (Fig. 7b). The back-scattered electron fractograph, displayed in Fig. 8b, demonstrates the finer microstructure of composite with darker and white phases as Al₂O₃ and ZrO₂, respectively, with small isolated pockets of voids.

Table 4

Mechanical properties of the optimized fully dense composite materials

Specimen	E (GPa)	H _v (GPa)	$\frac{K_{\rm IC}}{(\rm MPa\ m^{1/2})}$
$Al_2O_3-5 mol\%ZrO_2$	368.6	16.68 ± 0.7	4.89 ± 0.4
$(5 \text{ mol}\%\text{ZrO}_2 = 5.9 \text{ wt.}\% \text{ZrO}_2)$ WC-6 wt.% ZrO ₂ [22]	485.4	22.3 ± 0.5	5.4 ± 0.3



Fig. 9. X-ray mapping micrographs of different elements: (a) Al and (b) Zr of the fractured surface.



Fig. 10. Schematic representation of martensitic transformation of ZrO_2 particles within the alumina matrix (a) crack propagation during indentation fracture (b).

Table 4 shows the mechanical properties of the Al₂O₃-5 mol%ZrO₂ composite sintered at 1550 °C for 4 h. The composite exhibits hardness of ~17 GPa and moderate fracture toughness of 4.8 MPa $m^{1/2}$. Similarly, it is to be mention that WC-6 wt.% ZrO2 composite can exhibit a 22 GPa hardness and $\sim 5 \text{ MPa} \text{ m}^{1/2}$ fracture toughness [22]. The mechanical properties of the studied materials may be explained on the basis of the intrinsic properties of the two components, Al₂O₃ and ZrO₂. SEM observations also sustain the role of transformation toughening in these composites. Fig. 10a illustrates the schematic martensitic transformation mechanism during fracture [23]. Fig. 10b shows the propagation path of an indentation crack in the ZTA composite, which is experienced along the ZrO_2 particle cluster. Hence, K_{Ic} changes with the addition of ZrO₂ may be rationalized by the relative predominance of the toughening mechanism, i.e., zirconia phase transformation. For the zirconia content of the ZTA studied in this work, it seems that the extent of transformation toughening is more significant, leading to an effective increase of $K_{\rm Ic}$. Moreover, such transformability is also speculated to account for the reduction in hardness detected in the sintered ZTA composite, since hardness is inversely correlated with transformation easiness [24].

4. Conclusions

The present work reports the synthesis of ultra-fine Al_2O_3 -ZrO₂ powders (20–200 nm) through the sol-gel route. Hundred percent *t*-ZrO₂ can be found in the sintered body without the addition of any dopant at 1550 °C/4 h with ~98% densification. The fine ZrO₂ (100–300 nm) has been homogeneously dispersed within the alumina matrix with a maximum grain size of ~0.8 µm, which will increase the toughness of the alumina matrix. The indented fracture surface is associated with 15% *m*-ZrO₂ from *t*-ZrO₂.

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