

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 ZrO₂ particles, which was associated with *t*-ZrO₂ to *m*-ZrO₂ 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

ZrO₂) [2,3]. Homogeneous as well as fine dispersions of ZrO₂ 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)₃·9H₂O (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 Al₂O₃–ZrO₂ powder was prepared with a composition of 95Al₂O₃–5ZrO₂ (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

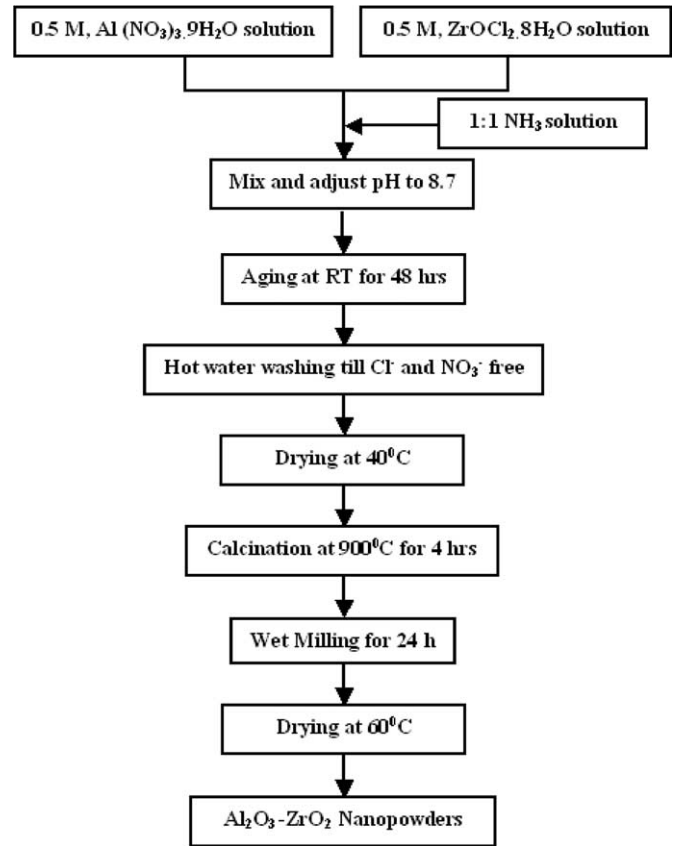


Fig. 1. The typical flow chart of the processing of Al₂O₃–ZrO₂ composite nano-powder.

size of 0.02° (2θ) 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:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

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 subtracted from the peak width before calculating the crystallite size using the following formula:

$$B^2 = B_{\text{meas}}^2 - B_{\text{Equip}}^2 \quad (2)$$

Then the as-synthesized Al₂O₃–ZrO₂ 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 computer-controlled 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 (∅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_{Ic} was measured by the indentation method, where the length of cracks emanating from the Vickers indentation corners. K_{Ic} was calculated using the expression proposed by Anstis et al. [12]:

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

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 pulse-echo 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]:

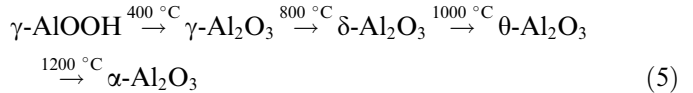
$$X_m = \frac{I_m(111) + I_m(11\bar{1})}{I_m(111) + I_m(11\bar{1}) + I_t(111)} \quad (4)$$

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 $t\text{-ZrO}_2$ [14]. The XRD analysis of calcined powder (300 °C for 8 h) also confirms the presence of the $t\text{-ZrO}_2$ phase. Again, the endothermic peak at 310 °C corresponds to the transformation of $Al(OH)_3$ and $\gamma\text{-AlOOH}$ into $\gamma\text{-alumina}$. 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 $\alpha\text{-Al}_2O_3$ completes at 1210 °C with a small exothermic peak [16]. The phase transformation from $\gamma\text{-AlOOH}$ to $\alpha\text{-Al}_2O_3$ follows the following path as reported by earlier researchers [17].



The reduction of specific volume to the extent of 24% is observed in the phase transformation of boehmite (0.332 cc/g) to $\alpha\text{-Al}_2O_3$ (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 $\delta\text{-Al}_2O_3$ and $\theta\text{-Al}_2O_3$, and amorphous ZrO_2 formed during gel formation is transformed into $m\text{-ZrO}_2$ and $t\text{-ZrO}_2$ (Fig. 2 and Table 1). The broadening of peaks in XRD patterns con-

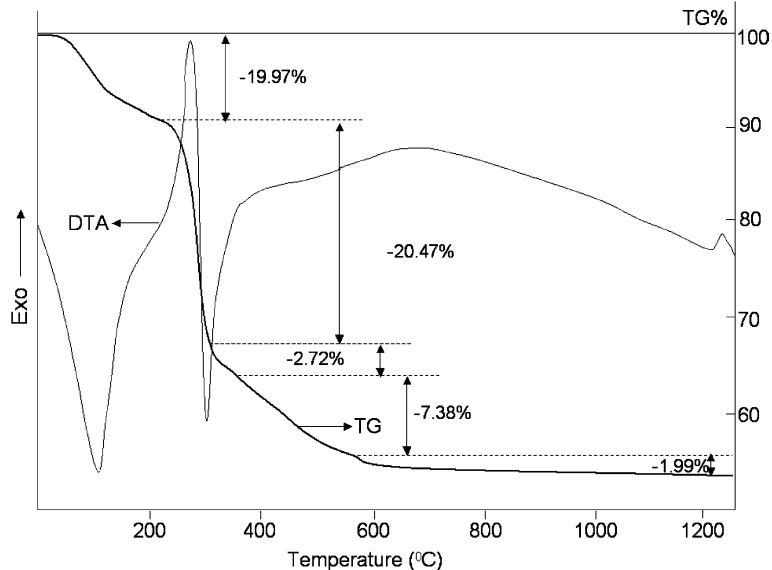


Fig. 2. TG/DTA plot for the $Al_2O_3\text{-ZrO}_2$ precursor powders in air.

