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Three different alumina–zirconia composites: Sintering, microstructure and mechanical properties

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Two commercial 3 mol% yttria–partially stabilized zirconia powders, with 0.3 wt% Al_2O_3 (Y–PSZA) and without Al_2O_3 (Y–PSZ), and a Zr (IV) precursor were used to produce alumina (Al_2O_3)–zirconia (ZrO_2) slip cast composites. The influence of both the zirconia content and the reduction of zirconia particle size on the sintering behavior, microstructure development and mechanical properties were investigated. The increase in the zirconia content from 10.5 to 22 vol% increased the hardness; whereas, above 22 vol% ZrO_2 the hardness decreased. A significant increase in the fracture toughness with increasing the ZrO_2 content over 22 vol% was obtained by the stress-induced phase transformation. The flaw size limited the strength below 22 vol%; whereas, above 22 vol% ZrO_2 the strength was controlled by the stress-activated phase transformation. For 10.5 vol% ZrO_2, the smaller ZrO_2 grains produced by using the Zr (IV) precursor were more effective in preventing the Al_2O_3 grain growth resulting in higher hardness. However, the tetragonal–monoclinic (t–m) transformation of some unstabilized ZrO_2 grains during cooling reduced Young's modulus and fracture toughness.

1. Introduction

The mechanical behavior of zirconia-toughened-alumina ceramics is currently of great interest, mainly as a result of their high strength and enhanced fracture toughness [1]. The stress-induced martensitic transformation of tetragonal zirconia can markedly increase the fracture toughness of alumina–zirconia ceramics. In order to retain the tetragonal phase to room temperature, it is found that both the addition of Y_2O_3 stabilizer and the reduction of ZrO_2 grain size are required [2]. In this work, two commercial 3 mol% yttria–partially stabilized zirconia powders, with 0.3 wt% Al_2O_3 (Y–PSZA) and without Al_2O_3 (Y–PSZ), were used to produce Al_2O_3–ZrO_2 slip cast composites. The Al_2O_3 content play an important role for the densification of Y–PSZ ceramics. Matsui [3] explained the enhanced effect of Al_2O_3 on the densification of Y–PSZ with a change of the principal diffusion mechanism from grain-boundary to bulk volume diffusion. We have also studied [4] the enhanced sintering effect of Y–PSZ with 0.3 wt% Al_2O_3 compared to Y–PSZ in the sintering of 50 vol% Al_2O_3–50 vol% ZrO_2 composites.

Al_2O_3 and ZrO_2 ceramics can be produced by conventional powder processing techniques which involve mixing, pressing and subsequent sintering. Slip casting is a suitable consolidation process to obtain compacts with high sintered densities and microstructural homogeneity allowing the manufacture of components with complex shapes [1]. According to Requena et al. [5] the slip casting technique is a powerful method to obtain Al_2O_3 and Al_2O_3/ZrO_2 multilayer composites with nearly theoretical density ($>98\%$).

In a recent paper we reduced the ZrO_2 particle size by using a Zr (IV) precursor route [6]; smaller particles with respect to the classical powder mixing route, homogeneously distributed on the Al_2O_3 particle surfaces were obtained. Szutkowska [7] studied the fracture resistance behavior of sintered alumina–10 wt% zirconia (≈ 7 vol% ZrO_2) produced either with unstabilized ZrO_2 or 3 mol% yttria–partially stabilized zirconia powders; he measured the fracture toughness of these composites and pure alumina by different methods. His results showed that the alumina–10 wt% zirconia composites with unstabilized ZrO_2 had the highest fracture toughness value independently on the used method. In this paper, a series of Al_2O_3–ZrO_2 formulations were prepared either by using the two commercial 3 mol% Y–PSZ powders or a Zr (IV) precursor. The influence of both the zirconia content and the reduction of zirconia particle size on the sintering behavior and microstructure

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development were studied. In addition, the effect of these microstructures on the mechanical properties were discussed.

2. Experimental procedure

2.1. Raw materials and powder processing

Alumina (A16 SG, Alcoa Chemicals, USA, $d_{50}=0.40$ μm), 3 mol% yttria–partially stabilized zirconia with 0.3 wt% Al_2O_3 (Saint-Gobain ZirPro, CY3Z-MA, Chine, $d_{50}=0.23$ μm) and without Al_2O_3 (Saint-Gobain ZirPro, CY3Z-NS, Chine, $d_{50}=0.64$ μm) powders were used in this study. For the colloidal method, zirconium (IV)-propoxide solution (70 wt% in 1-propanol) (Sigma-Aldrich, Ireland) was added dropwise to a stable alumina (A16) suspension in absolute ethanol; this method was described in a previous paper [6]. The compositions used to prepare Al_2O_3–ZrO_2 composites are summarized in Table 1.

A commercial ammonium polyacrylate solution (NH_4PA) (Duramax D 3500, Rohm and Haas, Philadelphia PA) was used as deflocculant. 48 vol% aqueous Al_2O_3–ZrO_2 suspensions with the different compositions (Table 1) and the optimum NH_4PA concentration were prepared by suspending particles in deionized water via 40 min of ultrasound; the pH was manually adjusted to be maintained at 9 with ammonia (25%). Slips were cast in plaster molds into rectangular bars ($12\times10\times9$ mm^3); the consolidated bars were dried slowly in air for 24 h at room temperature and 24 h at 100 °C. The green samples were sintered in air at 1100–1600 °C for 2 h (heating rate 5 °C/min).

2.2. Characterization techniques

The specific surface area (S_g) and the particle size distribution of the powders were measured using a Micromeritics Accusorb and a Sedigraph (Micromeritics), respectively.

The density of the green compacts was determined by the Archimedes method using mercury displacement. The bulk density of the sintered samples was determined by water immersion (Standard Method ASTM C20). An impulse excitation frequency tester (GrindoSonic, MK5 Model) was used to determine the Young's modulus. The measured resonant frequency, along with the length, thickness, wide and weight of the bars were used in the following equation to calculate Young's modulus:

$$E = 0.9465\left(\frac{mf_f^2}{w}\right)*\left(\frac{L^3}{e^3}\right)*T_1 \tag{1}$$

where m is the specimen mass, w is the wide, L is the length, f_f is the frequency (Hz), e is the specimen thickness and T_1 is the shape factor (depedent on Poisson's ratio). Five measurements were tested for each sample and the results are presented as mean values. Theoretical values of Young's modulus were determined for comparison using a rule of mixtures in the form $E=E_1\nu_1+E_2\nu_2$; where E_1 and ν_1 are the modulus values and volume fraction of Al_2O_3, respectively, and E_2 and ν_2 are the respective values of ZrO_2.

The mechanical properties evaluated for the samples sintered at 1600 °C were hardness, fracture toughness (K_{1c}) and flexural strength. The sintered samples were polished with a series of diamond pastes down to 1/4 μm and annealed at 1100 °C for 30 min to remove surface strains introduced during machining. The Vickers hardness (Hv) was carried out using a diamond indenter (Buehler hardness tester) and calculated as follows:

$$\mathrm{Hv} = 1.854\frac{F}{d^2} \tag{2}$$

where F is the indentation load and d is the arithmetic mean of two diagonals (d_1 and d_2). 10 Hv measurements were used to obtain an average value.

The fracture toughness (K_{1c}) was calculated on the basis of the indentation method:

$$K_{1C} = 0.016\left(\frac{E}{\mathrm{Hv}}\right)^{1/2}\frac{P}{C^{3/2}} \tag{3}$$

where E is Young's modulus, Hv is the vickers hardness, P is the indentation load and C is the crack length, which was measured using the ocular on the hardness tester. The flexural strength of the sintered samples was measured using a three-point bending test (INSTRON, 4483). About 10 measurements of fracture toughness and flexural strength were tested for each sample and the results are presented as mean values.

The alumina and zirconia grain sizes were measured using SEM micrographs (JEOL, JSM-6360) of polished and thermally etched surfaces. The grain size values were the average of about a hundred measurements.

The percentages of monoclinic and tetragonal ZrO_2 in the composites were determined by XRD analysis (Philips 3020 equipment, with Cu-Kα radiation in Ni filter at 40 kV to 20 mA) using the Rietveld method [8].

Table 1
Compositions used for the preparation of Al_2O_3–ZrO_2 composites and green density of slip cast compacts.

Sample[a]	Al_2O_3 (vol%)	Y–PSZA (vol%)	Y–PSZ (vol%)	ZN (vol%)	Green density (% DT)[b]
10.5Y–PSZA	89.5	10.5	–	–	63.2
10.5Y–PSZ	89.5	–	10.5	–	64.3
10.5ZN	89.5	–	–	10.5	57.0
22Y–PSZA	78	22	–	–	62.5
22Y–PSZ	78	–	22	–	64.8
22ZN	78	–	–	22	54.0
50Y–PSZA	50	50	–	–	60.0
50Y–PSZ	50	–	50	–	65.3

[a] The numbers 10.5, 22 and 50 in the sample codes indicate the volume percent of zirconia in the composite.
[b] Theoretical density.

3. Results and discussion

3.1. Powder characterization

Fig. 1 a shows the particle size distribution curves of the Al_2O_3, Y–PSZ and Y–PSZA powders. In Fig. 1b the particle size distribution curves of the 10.5 and 22ZN powders after milling were compared with that of Al_2O_3. Alumina showed a unimodal distribution with particle diameters >0.1 and <0.75 μm, the more frequent particle diameters were in the range of 0.15–0.3 μm. A slightly narrow particle size distribution was found for Y–PSZA; thus a greater volume of finer particles (diameters between 0.10 and 0.20 μm) and a lesser volume of particles with diameters in the range of 0.20–0.55 μm were observed, the more frequent particle diameter was 0.15 μm. A bimodal distribution curve was found for Y–PSZ, the more frequent particle diameters (0.37 and 0.65 μm) were greater than those of Al_2O_3 and Y–PSZA powders.

A slightly wider particle size distribution was found for the ZN powders with respect to that of Al_2O_3 (Fig. 1b); a lesser volume of finer particles (<0.35 μm) and a greater volume of particles with diameters in the range of 0.35–0.9 μm were found. The more frequent particle diameters of 10.5ZN were in the same range as those of Al_2O_3; whereas, for the 22ZN powder the more frequent particle diameters became greater (0.40–0.60 μm). Although the Zr