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Aqueous Extrusion of Alumina–Zirconia (12 mol% Ceria) Composite using Boehmite as Extrusion Aid

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Abstract: Alumina–20 vol% zirconia (12 mol% ceria) composite powder has been extruded using boehmite (AlOOH) as an extrusion aid. A higher order of homogeneity of the constituent phases has been achieved in this work by controlling the pH of flocculation at 8.5. Sintering was carried out at 1600°C. The microstructural evaluation confirms uniform distribution of different phases throughout the specimen. The possibility of boehmite being used as extrusion aid to alumina based ceramics is highlighted. © 1998 Published by Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Out of the many ceramic fabrication techniques, extrusion is considered to be the most suitable method for producing a variety of shapes with constant cross-section. The ability to produce long wires/tapes from ceramic powder mixture[1] has initiated new fabrication routes for super conducting ceramics[2–4] ceramic composites[5] and piezoelectric materials.[6] The extrusion of viscous pastes has become increasingly important due to the advantages of formation of products at low temperature and pressure.[7] Recent reports highlight the use of inorganic binders[8] in view of their advantages of less binder burn-out problems and carbon residues. Monohydroxy aluminium oxide (boehmite) has been successfully indicated as extrusion aid for alumina systems[9,10] The effectiveness of boehmite as a binder as well as a reactive sintering aid has been reported,[11] highlighting the fact that boehmite derived alumina[1] becomes part of the matrix and thus avoids any possible residual impurities.

The major problem encountered in mixing multimodal slurries, where the components have different densities and surface charges, are the differential settling of particles causing inhomogeneity in the matrix and thus resulting in poor mechanical properties. Earlier reports suggest the possibility of keeping ceramic particles colloidally stable in ZrO_2 based composites by keeping high zeta potentials, preferentially at pH values less than 4[12,13] where a high potential minimises particle agglomeration and ensures stability to particle suspension. Preferably, the suspension should be colloidally stable and zeta potentials of the particles of precursor composite be of the same sign but should differ in their magnitude in order to achieve acceptable homogenisation.[13]

Alumina–20 vol% zirconia (12 mol% ceria) system has been studied extensively[14] and has been found that such composites possess a combination of high fracture resistance ($\sim$12.3 MPa$\sqrt{m}$) and strength ($\sim$900 MPa) by suitably controlling the zirconia and alumina grain sizes during sintering of colloidally processed green pieces.[15]

The present investigation reports the preparation of Al_2O_3–20 vol% ZrO_2 (12 mol% CeO_2) composite precursor, the extrusion features, sintering and microstructure development. The advantages of using boehmite as a binder and extrusion aid are highlighted. A comparison of microstructures of the sintered extruded sample is made with that of uniaxially pressed sample (without boehmite).

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2 EXPERIMENTAL

Ceria and zirconia powders of purity 99.7% were supplied by M/s. Indian Rare Earths Ltd., India. Aluminium nitrate (AR grade) was supplied by M/s. Qualigens, India.

A batch of 200 g 12 mol% ceria–zirconia mixture (Ce–Zr) was prepared by mixing 32 g ceria powder with 168 g of zirconia powder and ball milling for 48 h with Ce–TZP grinding balls in propan-2-ol medium. The mixture was concentrated over a steam bath to a viscous slurry and was then dried in an oven and further deagglomerated in an electric mortar grinder for 30 min. Tap density of the mixture was measured (Densitometer, India).

Boehmite was prepared from aluminium nitrate as described elsewhere,[16] and was characterised by thermogravimetric and differential thermal (TGA and DTA) measurements (TGA 50 H and DTA 50H, Shimadzu Corporation, Japan).

α-alumina powder was prepared by calcining boehmite powder at 1250°C for 5 h, further ball-milling for 48 h using alumina balls and then characterised by tap density and XRD (Dmax/2C, Rigaku, Japan).

2.1 *Preparation of 20 vol% Ce–Zr–alumina composite powder (Ce–Zr–Al)*

100 g of Ce-Zr-Al was prepared by mixing 63.12 g of α-alumina with 26.8 g of Ce–Zr powder in a poly vinyl chloride container and ball milling for 24 h in propan-2-ol medium using Ce–TZP balls. The slurry was dried at 90°C for 24 h in a hot air oven followed by deagglomeration in an electric mortar grinder for 30 min. The composite powder was characterised for tap density and DTA. A part of this composite powder (Ce–Zr–Al) was uniaxially pressed at 200 MPa to 8 mm dia cylindrical pellets, for comparison with extruded samples.

2.2 *Preparation of 14 wt% boehmite–(Ce–Zr–Al) mixture (B–Ce–Zr–Al) for extrusion*

Boehmite was dispersed in double distilled water using a high speed stirrer and pH of the system was maintained at 3.5 by the slow addition of diluted HNO_3 till a stable sol was obtained. Ce–Zr–Al powder was added to the sol such that boehmite makes 14 wt% of the total powder mixture. A typical batch contained 63.12 g of α-alumina, 26.8 g Ce–Zr and 14 g boehmite. After stirring for 1 h, pH of the slurry was slowly raised to 5 by adding diluted. NH_4OH. Slurry was then ball milled for 8 h using alumina balls followed by stirring in a beaker and raising the pH to 8.5 by the addition of diluted NH_4OH. The slurry was consolidated at ~80°C to an extrudable consistency on a rectangular tray (50×40 cm) to ensure uniform drying.

Extrusion was carried out in a laboratory scale plunger type extruder to 8 mm rods. Extrudate was dried using a humidity controlled oven (Remi, Environmental Test Chamber, India) at 65% RH and 45°C. Both extruded and uniaxially pressed samples were sintered at 1600°C for 2 h under identical conditions (Nabertherm, Germany).

3 RESULTS AND DISCUSSION

3.1 *Powder characterisation*

Figure 1 shows the DTA curve of the boehmite used in this experiment. The initial endotherm below 100°C is due to the evolution of the free water in boehmite. The endotherm at 457°C indicates the formation of γ-alumina and exotherm at ~1200°C represents transformation to α-alumina. The broad exotherm in the range 500–1000°C is indicative of the formation of various transition alumina phases before conversion to α-alumina. In the thermogravimetric analysis curve (Fig. 2), the initial loss corresponds to loss of adsorbed water. About 80% of the weight loss takes place at below 500°C and the remaining by ~700°C. However, the weight loss is over a wide range of temperature and hence the heat schedule needs to be adjusted for debinding accordingly. Figure 3(a) shows the tap density curve for α-alumina. The maximum tap density obtained was about 25.12% of the theoretical density.

Figure 4(a) shows the DTA of the Ce–Zr powder. The peak at ~1182°C may be indicative of the m→t transformation of zirconia. The average grain size of Ce–Zr powder was ~4 µm. Figure 3(b) shows the tap density of the powder to be 34.36% of the theoretical density.

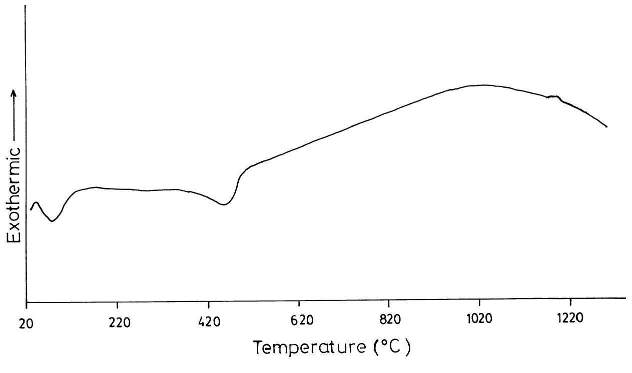


Fig. 1. Differential thermal analysis curve of boehmite.

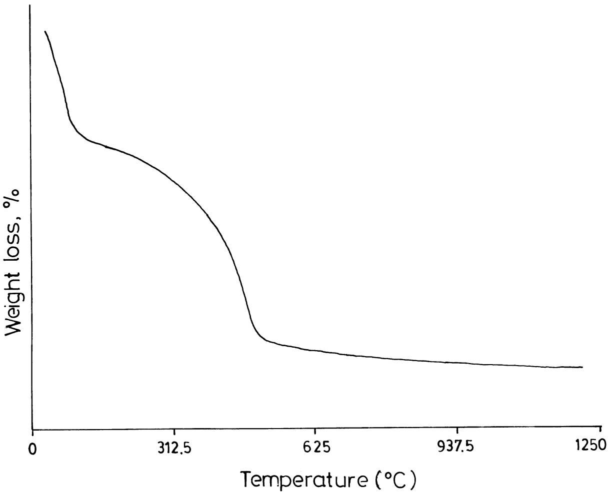


Fig. 2. Thermal analysis curve of boehmite.

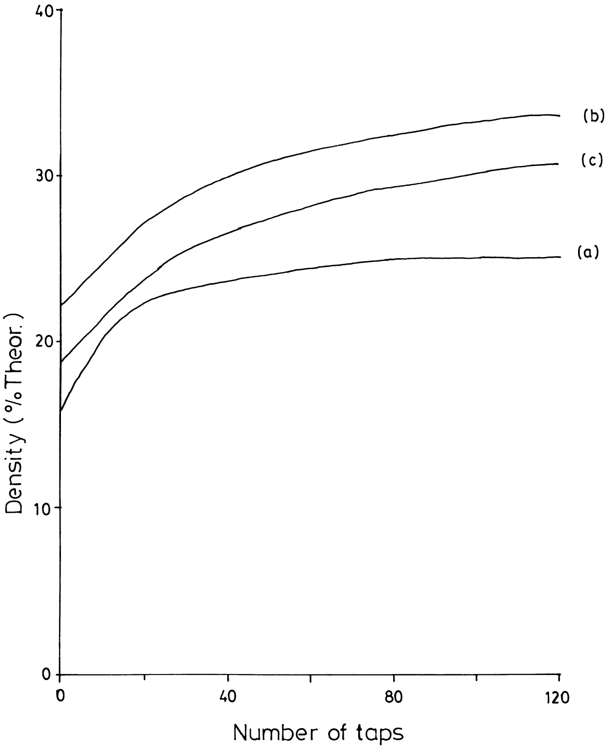


Fig. 3. Tap density curves of (a) α-alumina (b) Ce–Zr (c) Ce–Zr–Al.

The tap density of the Ce–Zr–Al powder (Fig. 3(c)) was 31.3% of the theoretical density. The particle packing has improved considerably by the addition of Ce–Zr to α-alumina. The exotherm at ~1170 (Fig. 4(b)) indicates the m→t transformation. The uniaxially pressed compact (at ~200 MPa) after sintering at 1600°C for 2 h has yielded around 94% theoretical density.

The DTA of the dried powder of B–Ce–Zr–Al shows an endotherm at ~460°C (Fig. 4(c)), which is obviously the γ-alumina formation of boehmite. Here the m→t transformation is represented by a smooth exotherm from 1150 to 1200°C.

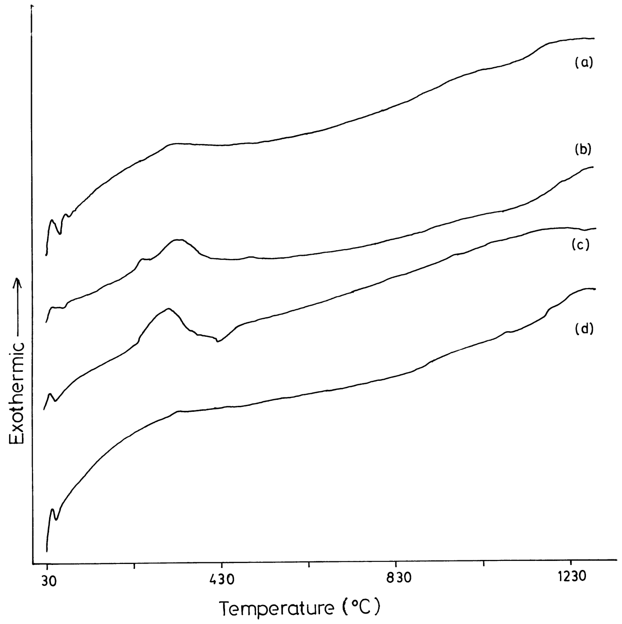


Fig. 4. Differential thermal analysis curves of (a) Ce–Zr (b) Ce–Zr–Al (c) B–Ce–Zr–Al (d) Zirconia.

3.2 Boehmite–Ce–Zr–Al system (B–Ce–Zr–Al)

The percentage of boehmite was fixed at 14 wt% of the total powder mixture, based on the torque rheology carried out on an alumina system.[11] The major problem encountered in mixing of multimodal slurry of varying densities is the differential settling of the particles. Hence a uniform distribution of grains is difficult to be achieved. A flocculated state is suggested in such occasions.[13,17] The initial dispersion of the composite powder was done in boehmite at pH 4, where the surface charge in the particles was maintained higher. The pH of the suspension has been raised to 5 in order to bring the surface charge low, but still to keep the zeta potential on the same side. Further ball milling at this pH facilitates an intimate coating of boehmite over the Ce–Zr–Al particles and ensure uniform distribution of boehmite in the mixture. The pH of slurry was further raised to 8.5 under intense stirring condition in order to avoid any settling of the particles. The composite particles are expected to be entrapped in the boehmite gel matrix at this stage. The consolidated mass used for extrusion contained about 18 wt% moisture. While the particulates of alumina and zirconia–ceria mixture are many times greater than the boehmite nano particles, there appears sufficient possibility for the boehmite particles to fill in the groups created by the packing of the large ones, similar to the situation where a mixture of boehmite and fine alumina particles are experimental as coatings for composites.[18] The boehmite gel has also been indicated to be an excellent binder for the coated particles.

3.3 Dehydroxylation and sintering

Thermomechanical analysis of the extruded B–Ce–Zr–Al is presented in Fig. 5. A small shrinkage is noted around 450°C corresponding to the γ-alumina conversion of the boehmite. The major shrinkage starts at around 1180°C which is characteristic of the m→t transformation of zirconia as evidenced from the DTA (Fig. 4(b)). Further shrinkage indicates the sintering of the sample.

The dehydroxylation and sintering schedules were formulated based on the TGA of boehmite and TMA of the composite precursor.

The schedule adopted was
RT→300°C ($2°\mathrm{min}^{-1}$)→700°C ($5°\mathrm{min}^{-1}$)→1600°C ($10°\mathrm{min}^{-1}$) 2 h soaking.

Sintered densities obtained for extruded samples were above 98% whereas that of Ce–Zr–Al powder compact was around 94%.

3.4 Microstructural features

Figure 6(a) shows the fractograph of the sintered extruded sample which appears to be nearly fully dense with an average grain size of ~3 µm. The grains appear to be well distributed without any significant variation in grain size indicating a reactive sintering of boehmite to form part of the matrix.

In the fractograph of Ce–Zr–Al pellets (Fig. 6(b)), average particle size appears to be greater than its extruded counterpart. Intergranular cracks were seen in the sample. Certain inhomogeneous distribution of phases is also noted. This can be the reason for its lower density. Figure 6(b) also reveals intragranular fracture mode.

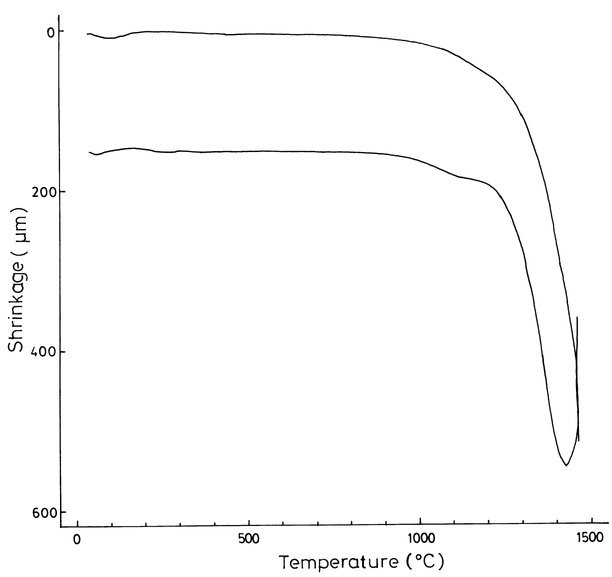
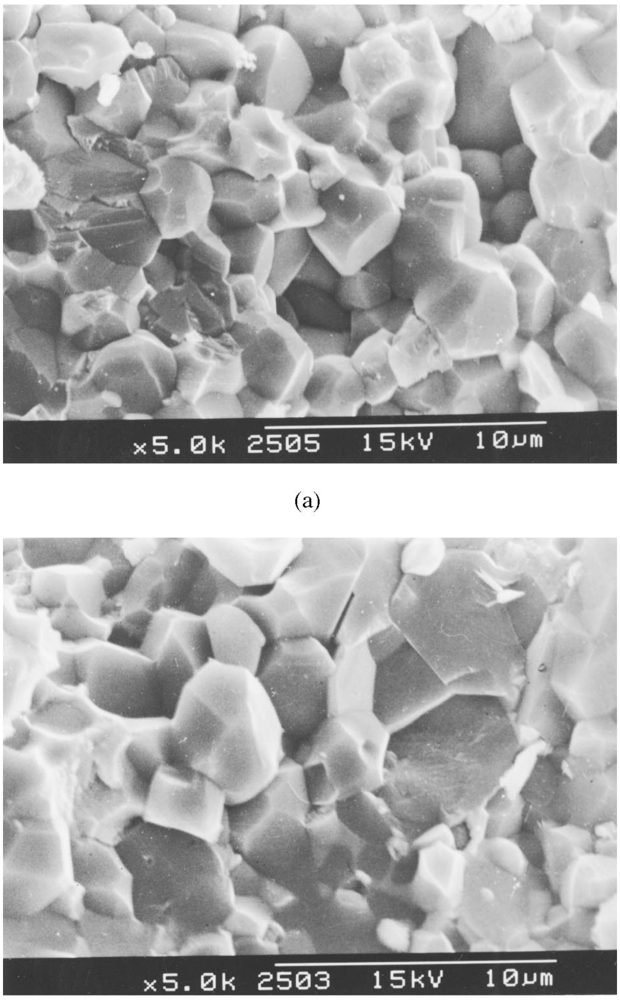


Fig. 5. Thermomechanical curves of extruded B–Ce–Zr–Al (green).



(a)

(b)

Fig. 6. Fractographs of (a) B–Ce–Zr–Al extruded sample (b) Ce–Zr–Al pellet.

4 CONCLUSION

20 vol% zirconia (12 mol% ceria)–alumina composite has successfully been extruded using boehmite as a vehicle for extrusion. Densities obtained for extruded samples were >98% whereas that of uniaxially pressed samples were ~94%. Addition of boehmite to the composite precursor has improved the particle packing as well as the sintered density. Differential settling of particles were not seen. Hence it can be concluded that boehmite is a promising extrusion and sintering aid for alumina-based ceramics.

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