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Colloidal Processing of Sol-Sprayed Ceramic Particulate Composites

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Abstract

Sol–gel based preparative procedures are capable of reducing the problems of particle size distribution, purity and homogeneity of the phases in ceramic particulate composites. However, the tendency for agglomeration of these powders creates serious problems for processing to shapes. The present work is a critical study of the preparation of 10% ceria–alumina composite particulates, by a mixed sol-spray technique followed by pressure filtration for final consolidation. The powder was also compacted by ceramic uniaxial dry pressing for comparison purposes. The details of powder preparation, powder characteristics, filtration conditions, compaction and sintering behaviour and the final sintered microstructural features of the compacts have been studied and evaluated.

Auf Solgel basierende Verfahren ermöglichen eine Verbesserung der folgenden Punkte: Teilchengrößenverteilung, Reinheit und Homogenität der Phasen in aus Partikeln bestehenden Verbundwerkstoffen. Jedoch führt die Neigung dieser Pulver zur Bildung von Agglomeraten zu erheblichen Schwierigkeiten bei der Herstellung von Formen. Die vorliegende Arbeit ist eine kritische Untersuchung der Präparation einer 10% Zeriumoxid–Aluminiumoxid Verbundmischung. Die Präparation erfolgte durch eine gemischte Solspritztechnik gefolgt von einer Preßfiltration zur abschließenden Verdichtung. Zu Vergleichszwecken wurde das Pulver auch durch keramisches, einachsiges Trockenpressen verdichtet. Die Einzelheiten der Pulverherstellung, der Pulvercharakterisierung, der Filtrationsbedingungen, des Verdichtungs- und Sinterverhaltens und das mikrostrukturelle Erscheinungsbild nach dem abschließenden Sintern wurden untersucht und ausgewertet.

Les procédés de préparation basés sur les sol–gel devraient potentiellement permettre de réduire les problèmes de distribution granulométrique, de pureté et d'homogénéité des phases dans les composites à dispersion de particules. Cependant, la tendance à l'agglomération de ces poudres crée de sérieux problèmes à la mise en forme. Le présent travail consiste en une étude critique de la préparation de composites à particules à matrice alumine et contenant 10% d'oxyde de cérium. Les préparations ont été réalisées par une technique mixte de dispersion d'un sol, suivie d'une filtration sous pression pour la consolidation finale. La poudre a aussi été compactée par pressage uniaxial, dans un but comparatif. Les détails de la préparation de la poudre, ses caractéristiques, les conditions de filtration, le comportement à la compaction et au frittage ainsi que les caractéristiques microstructurales finales du fritté sont etudiés et discutés.

1 Introduction

In order to improve the toughness of alumina, many techniques for introducing second phase materials such as fibres, whiskers and hard particulates as possible toughening agents have been investigated.[1] Transformation toughening[2,3] and crack deflection or bridging[4,5] are known toughening mechanisms in ceramic composites. Recently, cubic ceria with high hardness was incorporated in zirconia ceramics for phase stabilisation[6] and in alumina–zirconia systems for second phase pinning.[7] The present

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authors have prepared alumina–ceria composite particulates by non-conventional routes.[8,9] Methods based on the preparation of metal nitrate sols followed by spray and calcination to oxides of single and multi-component systems are already reported.[10–12] The high degree of homogeneity and uniformity that can be achieved by the mixed sol method resulting from nano-level mixing is known.[13]

Even though sol–gel methods in general are well acclaimed for bringing down the agglomeration of fine particulates, owing to their high surface activity agglomerates still persist. The non-uniform shrinkage of these agglomerates on sintering results in abnormal grain growth and creation of voids.[14–17] While sufficient improvement has been made in powder preparation, green consolidation procedures are equally important in achieving high green and sintered densities to result in better mechanical properties.[18,19] Colloidal processing of deagglomerated suspensions has recently been attempted to obtain desirable green density and sinterability for such powders. Further, this route is relatively simple and has been found to result even in attaining sufficient particle orientation.[20–24] Out of a number of colloidal processing techniques available such as centrifuging or slipcasting, pressure filtration is the most effective resulting in uniform density distribution throughout the compact.[25]

In the present study, an attempt has been made to consolidate ceria–alumina composite powders prepared through the mixed sol-spray route, and by pressure filtration of a deagglomerated slurry at controlled rates. The sintering behaviour and microstructural features of the compacts thus produced are evaluated and compared with dry-pressed counterparts.

2 Experimental

The chemicals aluminium nitrate, hydrochloric acid, ammonium hydroxide and nitric acid were all AR grade supplied by BDH (Bombay, India). Cerium nitrate was supplied by M/s Indian Rare Earths Ltd (Kerala, India).

As a first step in the preparation of composite powders, mono-hydroxy aluminium oxide sol was prepared from a solution of aluminium nitrate (100 g) in double-distilled water. Hydroxides were precipitated by addition of 25% ammonia solution drop by drop at a pH of 8 at around 85°C. The precipitate was washed free of nitrates and then peptised by 0·3 molar nitric acid at a pH of 3·5. The sol concentration was adjusted to 3 mol/litre by evaporation.[11] Cerium hydroxide sol prepared in a similar manner[26] was also evaporated to give 0·1 mol/litre concentration. Over-concentration of the sols may result in agglomeration and hence was avoided.

The composite sol was prepared by mixing calculated quantities of the individual sols and adjusting the pH condition to a value of 2·9. This was then spray-dried in a mini-spray-drier (Buchi laboratoriums-technik AG, Switzerland), through a nozzle of 1 mm dia with a fixed inlet temperature of 175°C and outlet temperature of 105°C. The thermogravimetric analysis (TGA) of the sample was performed in a Dupont TGA (Dupont instruments, USA) at a constant heating rate of 10°C/min up to 1000°C. The calcination of the powder was done at 1000°C (rate 10°C) for 1 h. Particle size distributions of the samples were measured in a sedigraph 5000D particle size analyser (Micromeritics, USA). Compaction characteristics were studied in the uniaxial mode over the pressure range from 7·5 to 300 MPa. Compaction densities were calculated from ram displacement data measured at an accuracy of 0·02 mm. Tap densities were found in a powder densitometer and the dispersion stability of the dilute suspensions was measured by a nephelometer.

The slurry for pressure filtration at a concentration of 45 vol% solid was prepared by ball milling the composite powder in a PVC container in an aqueous medium at pH 3 for 12 h. The pH adjustments were made by addition of dilute hydrochloric acid. One part of the ball-milled slurry was used for pressure filtration studies. The other part after drying was pressed at 200 MPa to cylindrical pellets of 12·75 mm diameter and sintered.

Pressure filtration was done in a cylindrical die system having 12·75 mm diameter and similar in form to one reported in Ref. 27. Filtration was carried out through both the upper and lower surfaces, keeping the filters protected by two metallic shields. A thick filter was used in the lower side, in order to counteract gravity effects on filtration. A pressure of 5 MPa was applied initially during filtration and then increased to 80 MPa. Sintering was carried out on such samples after drying. Sintering studies were performed in a Nabertherm 1750°C furnace (Nabertherm, Germany). The microstructural observations were performed in a Jeol 35C scanning electron microscope.

3 Results

The concentration of alumina sol taken was 3 mol/litre and that of ceria 0·1 mol/litre. This particular ratio of concentrations of the individual sols provides a uniform distribution of ceria in alumina (10:90) in each microunit considered. The

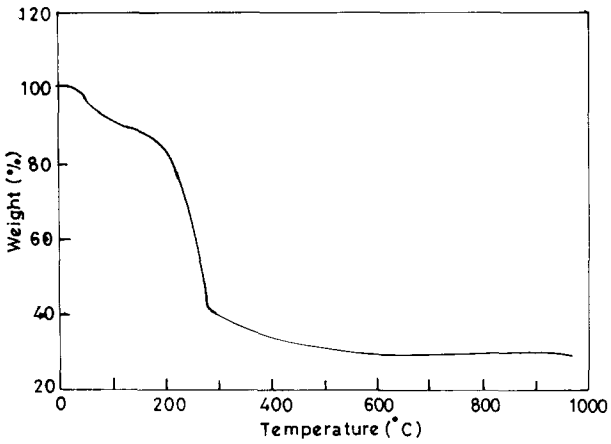


Fig. 1. TGA of the spray-dried sample.

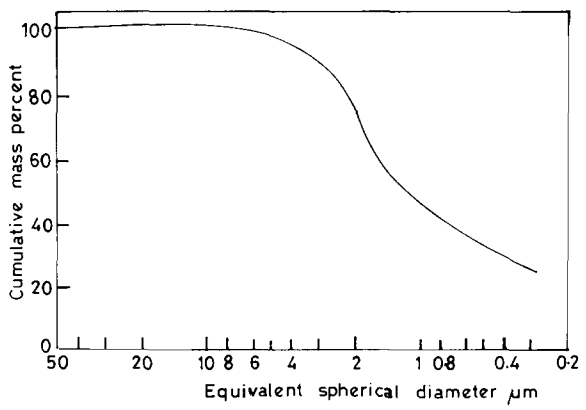


Fig. 3. Particle distribution curve of the composite sample.

usual method of mixing a salt solution to a matrix sol creates severe agglomeration problems resulting from the cementation of the salt on dehydration. The pH conditions were selected so as to give a very high surface positive charge for the Al–O–OH particles and comparatively lower surface charge for the hydrous ceria particles. This ensures homogenous mixing of the composites.[13,24] The TGA of the sample presented in Fig. 1 shows an early decomposition of around 10% moisture, followed by about 50% weight loss below 300°C. The major reduction would be attributed to the evaporation of occluded water in the gel structure and the decomposition of anion species. The decomposition is more gradual and almost steady after this, with a weight loss of around 10% (300–550°C). A separate analysis of ceria samples showed marginal losses of around 1–2% in the range of 550–900°C. In order to ensure full decomposition of the composite sol, a temperature of 1000°C was hence selected for calcination. The sample was heated at a constant rate of 10 C/min, up to 1000°C and kept for 1 h. X-ray analysis of the calcined sample revealed a pattern consisting of diffused alumina peaks along with sharp ones attributed to cubic ceria. Figure 2 gives the X-ray diffraction (XRD) patterns of the calcined composite sample (Fig. 2(b)), along with a boehmite sample calcined in the same environment (Fig. 2(a)), However, calcination at 1100°C develops an α-alumina phase as is shown in the XRD pattern in Fig. 2(c).

The cumulative average aggregate size of the powder was 1·2 μm (from Fig. 3). However, it is assumed that the actual crystallite sizes were much smaller possibly in the submicrometre range. The powder apparent density was measured from a highly dispersed slurry as 3·8 g/cm^3. This value is taken as 100% for all green density calculations. Figure 4 shows the progress of densification of the powder under a constant tapping force. A maximum tap density of 1·2 g/cm^3 (31%) has been obtained. The densification on compaction, as is seen in Fig. 4 reached a maximum of 50% at 300 MPa. The change in slope of the compaction response diagram suggests the presence of agglomerates or aggregates in the system[28,29] differing in strength and having different chemical and physical nature, introduced during preparation and calcination.

Figures 5 and 6 show the results of the light scattering experiments conducted on dispersed composite suspensions over a period of about 24 h. It is evident from the figure that between pH 2·8 and 4, the suspension is fairly stable without much sedimentation up to 3–4 h. Since the pressure

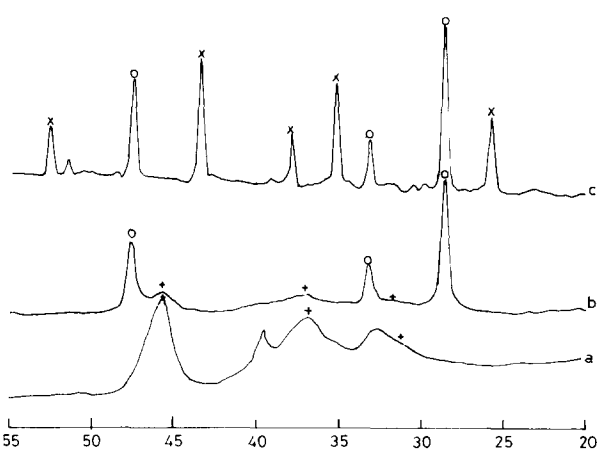


Fig. 2. XRD patterns of (a) alumina calcined at 1000°C; (b) alumina–ceria calcined at 1000°C; and (c) alumina–ceria calcined at 1100°C.

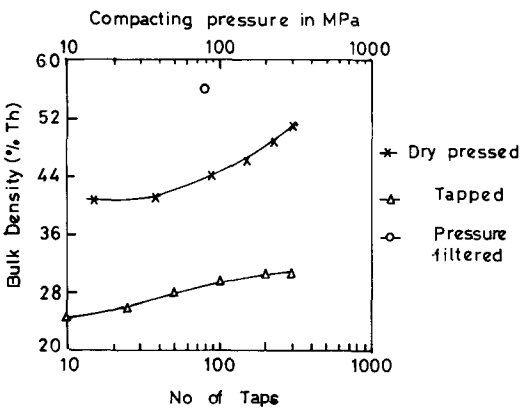


Fig. 4. Packing and compaction behaviour of the powder.

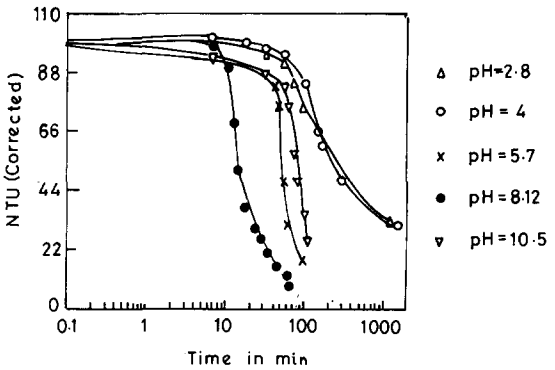


Fig. 5. Colloidal stability of the composite suspension with change in pH and time.

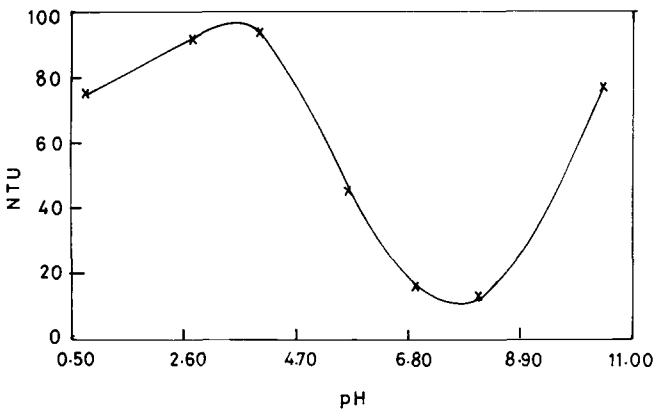


Fig. 6. Stability condition of the composite suspensions (initial NTU 100) after 1 h of dwelling.

filtration requires less than an hour, this ensures the stability of the suspension during pressing. Pressure filtration was conducted at around pH 3·15 to obtain densities which are pressure independent[23] taking care to avoid differential sedimentation causing mass segregation.[24,29] The high degree of stability of the suspension and the high volume fraction of solid loading involved (45 vol%) in the present case,[30] eliminates mass segregation by keeping the individual particle sedimentation velocity extremely low[30] while allowing moderate filtration rates.[29] A green density as high as 56% (Fig. 4) was achieved in the present work.

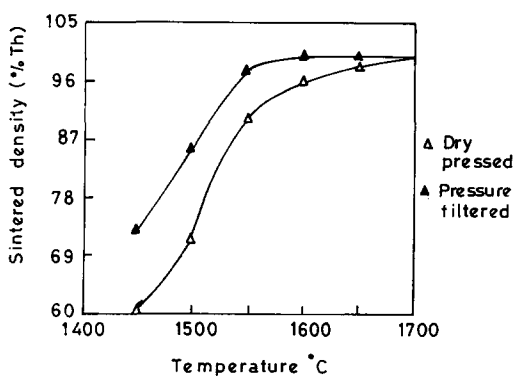
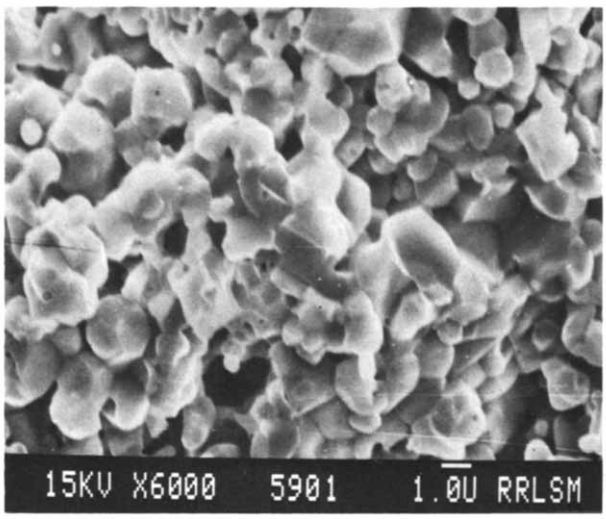
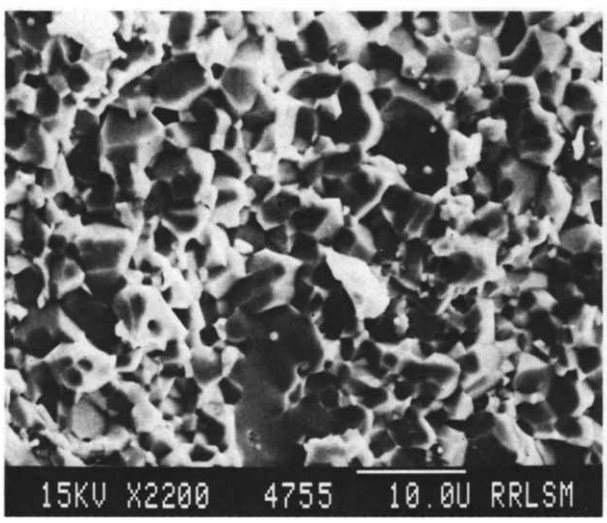


Fig. 7. Densification diagram of the samples.



(a)



(b)

Fig. 8. Micrographs of sintered samples: (a) dry-pressed; and (b) pressure filtered.

The densities of the dry-pressed (200 MPa) as well as pressure filtered samples sintered over the temperature range 1450–1700°C are shown in Fig. 7. Almost full densification can be achieved at a temperature of 1550°C for the pressure-filtered samples while it requires temperatures as high as 1700°C for the dry-pressed part.

Figure 8 shows micrographs of the sintered composite samples. There is sufficient localised agglomeration of the phases in the samples prepared by dry pressing and sintering at 1550°C (Fig. 8(a)). The average grain size is around 2·5 μm. The density of the sample was only 90%. On the other hand, pressure-filtered samples reached near theoretical values of the density at this temperature, with a final grain size of 2·5 μm (Fig. 8(b)). The homogeneous sintered microstructure may be a result of the uniform pore structure on the green compact giving effective second phase as well as uniform grain growth.[7,17]

4 Conclusions

(1) It was possible to prepare mixed composite powders with a satisfactory distribution of phases by resorting to a mixed sol-spray route.

(2) The sol–gel-derived composites prepared in this study could attain higher green as well as sintered densities when processed by the colloidal method.

(3) Colloidally processed sol–gel derived alumina–ceria composites could attain near theoretical density at 1550°C with an average grain size of 2·5 μm and also an even distribution of the ceria phase.

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