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Production of reactive single- and multi-component ceramic oxide powders and fabrication of high-strength ceramics

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Yttria-partially stabilized zirconia (Y-PSZ), alumina, mullite, Y-PSZ–Al_2O_3, alumina–zirconia and mullite–zirconia precursor powders were prepared by the hydroxide precipitation technique. The experimental conditions during precipitation were manipulated to produce homogeneous and reactive powders and examples of such variations are discussed. The formation of chemically bonded hard agglomerates was suppressed by dispersing the powders in isopropanol. The powders could be sintered to near-theoretical densities without sintering aids. The sintered bodies had very uniform microstructures and good mechanical properties. The fracture strengths of Y-PSZ, Y-PSZ–Al_2O_3, alumina, and mullite were over 1550, 2000, 625, and 350 MPa, respectively. Zirconia dispersions significantly improved the strengths of alumina and mullite.

1. Introduction

Oxide ceramic materials have a very important role in modern technology. However, their applications are critically dependent upon performance, which in turn depends on the intrinsic properties of the ceramics and on the microstructures of the sintered bodies. Fabrication of dense (near-theoretical density) bodies with little unwanted grain-boundary phase, small grain size, narrow grain-size distribution and uniform and homogeneous distribution of different component phases (in the case of multi-component systems) are essential to produce good structural ceramics [1–4].

The microstructural development of ceramics during firing and hence their performance depends on the characteristics of the precursor powders used in the fabrication process [2, 5]. Particle size, particle-size distribution, and the size, structure and nature of aggregates all play important roles in determining the microstructures of the sintered ceramics [6–8]. Wet chemical methods, though complex compared to conventional ceramic methods, are attractive for the production of precursor powders in a number of cases. This is because the experimental conditions during production of the powders can be manipulated to synthesize materials with unique properties which cannot be obtained by conventional ceramic methods. Therefore, a number of wet chemical methods have been developed over the years to produce reactive ceramic powders [9–12]. However, in most cases the powders produced were highly aggregated and inhomogeneous and further processing steps were essential to fabricate dense ceramics with good properties.

This paper emphasizes the importance of (1) choosing and maintaining the right experimental conditions during powder synthesis to produce homogeneous and reactive oxide powders, and (2) preparing powders containing weakly agglomerated crystallites. It is also shown that ceramics with enhanced properties can be fabricated by using powders prepared by a simple hydroxide precipitation method once the above conditions are satisfied.

2. Experimental procedure

The following three sets of structural ceramic materials were prepared by hydroxide coprecipitation technique.

1. Yttria-partially stabilized zirconia (Y-PSZ) and Y-PSZ–Al_2O_3 composites (ZYy–$XXAl_2O_3$).
2. Alumina and alumina–zirconia composites (A–$XXZYy$).
3. Mullite and mullite–zirconia composites (M–XXZ).

Here, ZYy is yttria zirconia alloy containing y mol % Y_2O_3, XX is wt % and A, M and Z are, respectively, alumina, mullite and zirconia.

The method of preparation and experimental conditions, characterization of powders and other results are reported in detail elsewhere [13–15] and are summarized only briefly here.

Standard solutions of zirconyl nitrate (zirconium carbonate dissolved in dilute nitric acid), yttrium nitrate (yttria dissolved in dilute nitric acid), aluminium nitrate and tetraethoxyorthosilicate were prepared. Required amounts of the standard solutions

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(concentration 0.4–0.6 M with respect to oxide content) were mixed and added to vigorously stirred (2000–2500 r.p.m.) ammonia solution (0.1–0.15 ml ammonia/ml water) in a nitrogen atmosphere. The precipitation was carried out relatively fast (about 100 ml min^{-1}) at room temperature. After the precipitation, the pH was adjusted to 9.0 and the slurry was stirred for another 60 min. Then the precipitates were filtered, washed repeatedly with deionized water, dispersed twice in acetone ultrasonically and dried in a vacuum oven at 70 °C for 24 h. Finally the oven-dried powders were dispersed and milled in iso-propanol for 24 h, dried and calcined at 900–1350 °C.

Differential thermal analysis (DTA) on 50 mg samples of the powders was done using a Stanton-Redcroft derivatograph operated in the range 20–1400 °C at a heating rate of 10 °C min^{-1}.

Surface-area measurements, X-ray diffraction and transmission electron microscopy were carried out on samples of the oven-dried coprecipitate that had been heated in air at several selected temperatures for 2 h.

Powder XRD patterns were recorded with a Rigaku diffractometer using filtered CuK_α radiation and a scanning rate of 2° min^{-1}.

Specimens for TEM were prepared by evaporation of an ethanolic dispersion of the powder on grids of perforated carbon film. They were examined in a Joel 100CX electron microscope.

Surface-area measurements were made by the BET method using nitrogen adsorption at − 193 °C using a "Sorptomatic" model instrument (Carlo Erba, Italy).

The oxide powders were cold-pressed into bars at 200 MPa and sintered in air between 1400 and 1700 °C for 2 h. The microstructures of the polished and thermally etched sintered ceramics were analysed by scanning electron microscopy (SEM). The fracture strength measurements were made in three-point bending with an outer span of 12.5 mm and a cross-head speed of 0.05 mm min^{-1}.

3. Results and discussion

3.1. Influence of experimental conditions in producing homogeneous precursor powders

Precipitation is the process during which both nucleation and growth of particles take place [16, 17]. Concentration of the solutions, pH before and after precipitation, temperature, impurities and other experimental conditions such as order and rate of mixing, rate of stirring, etc., are all critically important because they alter the equilibrium and non-equilibrium process of precipitation. Therefore, a slight change in any of the parameters involved during precipitation will change the characteristics of the precipitates formed. To illustrate this a number of coprecipitates of Y-PSZ–Al_2O_3 powders were prepared using different sets of experimental conditions. Here the influence of rate of stirring during precipitation in changing the characteristics of the powders is discussed.

Two coprecipitates of ZY2.5–30Al_2O_3 (S1 and S2) were prepared by the method described above. However, the rate of stirring during precipitation was 2000 r.p.m. for S1 and 500 r.p.m. for S2.

The DTA curve of S1 has an exothermic peak at 920 °C while the corresponding peak for S2 is at 820 °C (Fig. 1). The curve for S2 has an additional endothermic peak at 270 °C which is absent for S1. X-ray and electron diffraction studies of the powders calcined at different temperatures revealed that the exothermic peaks are due to crystallization of tetragonal zirconia and that the endothermic peak for S2 is due to dehydration of hydrous alumina.

The surface areas of S1 and S2 after calcination at 1000 °C for 2 h were, respectively, 53 and 23 m^2 g^{-1}.

Microstructural analyses revealed that alumina grains were distributed more uniformly in sintered S1 than in sintered S2 (Fig. 2b and c).

The stirring rate during precipitation changes local supersaturation conditions and thence the number of nuclei formed. Therefore, in the case of a multi-component systems the particle and agglomerate size of the precipitate and the distribution of different component phases will vary with stirring rate.

Faster stirring favours nucleation rather than growth and hence precipitates containing finer particles with a more homogeneous distribution of component phases will occur in rapidly stirred solutions compared to unstirred or slowly stirred solutions. Partial segregation of phases is common and cannot be totally avoided when precipitation methods are used to prepare multi-component powders [17]. However, the extent of segregation can be controlled by adjusting the experimental conditions, especially conditions which favour nucleation; this is because segregation is expected to take place during growth of

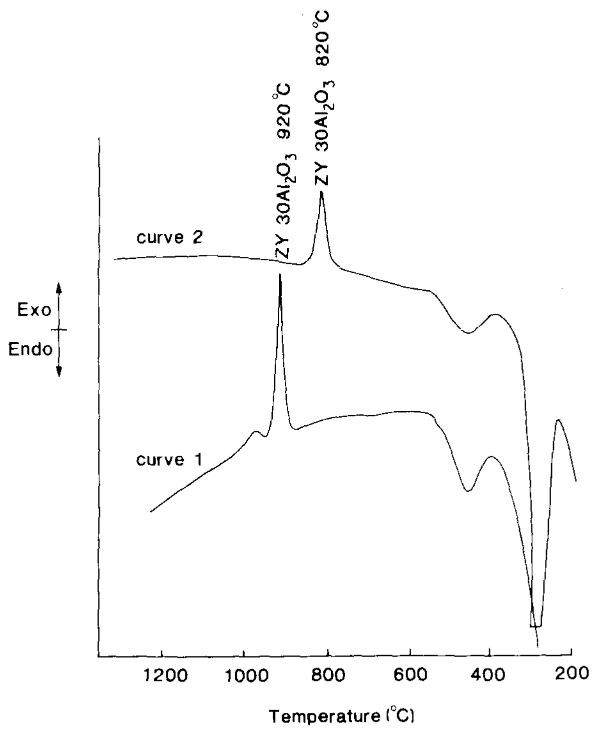


Figure 1 Differential thermal analysis (DTA) curves of oven-dried ZY2.5–30Al_2O_3 specimen prepared under two different experimental conditions.

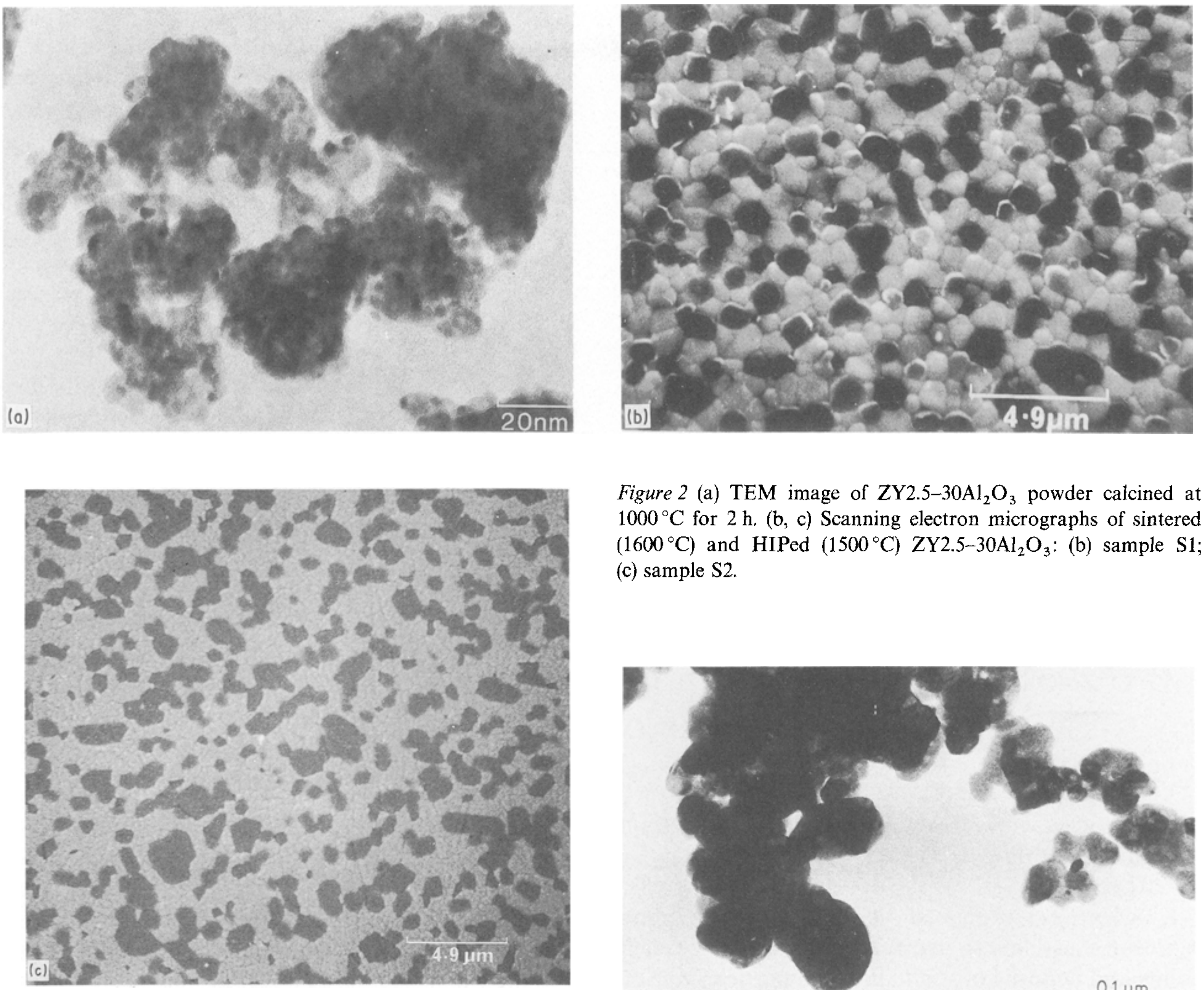


Figure 2 (a) TEM image of ZY2.5–30Al_2O_3 powder calcined at 1000 °C for 2 h. (b, c) Scanning electron micrographs of sintered (1600 °C) and HIPed (1500 °C) ZY2.5–30Al_2O_3: (b) sample S1; (c) sample S2.

particles as the growth process is diffusion controlled. The results of this paper illustrate the critical influence of experimental conditions, in particular the rate of stirring, in producing homogeneous ZY2.5–30Al_2O_3 powder by the hydroxide coprecipitation technique.

The micrographs shown in Fig. 2b and c reveal that the ceramic obtained from powder S1 has a more uniform distribution of alumina than the ceramic from S2 and this suggests that the distribution of alumina is more uniform in powder S1 than in powder S2. Therefore, the differences in the DTA and surface area results for the powders S1 and S2 can be explained by the differences in the distribution of alumina in the precipitated and calcined powders.

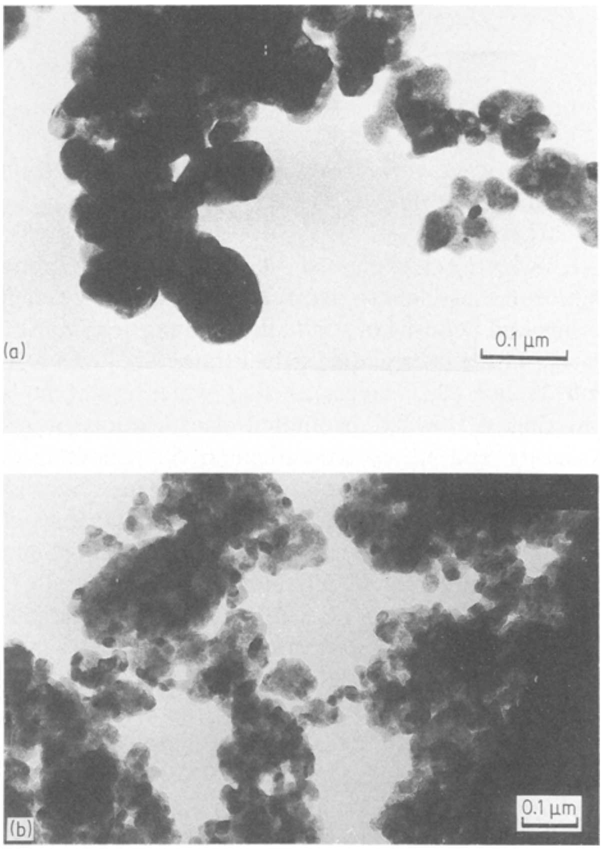


Figure 3 TEM images of coprecipitated ZY2.5–5Al_2O_3 specimen calcined at 1000 °C for 2 h; (a) calcined, and (b) precipitated powder dispersed in iso-propanol first and then calcined.

3.2. Production of readily sinterable precursor powders

In this section the sintering characteristics of powders containing aggregates of strongly bonded crystallites, the possible explanation for the formation of such aggregates during calcination of the precipitated powders and a method of producing weakly agglomerated sinterable powders are discussed.

Oven-dried coprecipitate of ZY2.5–5Al_2O_3, prepared by the method described in Section 2, was divided into two portions. One portion was calcined at 1000 °C for 2 h (powder S3) and the other portion was milled in iso-propanol for 24 h, dried and calcined at the same temperature (1000 °C for 2 h, powder S4). Transmission electron micrographs of the powders are given in Fig. 3a and b. Fig. 3a shows strongly aggregated crystals (size > 100 nm) along with weakly agglomerated crystallites (size < 20 nm) while Fig. 3b shows a uniform microstructure of crystallite size of 20–40 nm. The crystals of powder S3 have intra-agglomerate pores which tend to grow on subsequent calcination at higher temperatures. The crystals in the milled powders are uniform in size and they do not seem to contain many pores.

Cold-pressed powder S3 was found not to be sintered to more than 90% theoretical density even at 1700 °C, whereas the powder S4 could be sintered to close to theoretical density at 1450 °C. Scanning electron micrographs from the sintered (1600 °C for 2 h) ceramics are given in Fig. 4a and b for S3 and S4, respectively. Fig. 4a shows large isolated pores and non-uniform grain growth whereas Fig. 4b shows a uniform grain-size microstructure with no pores.

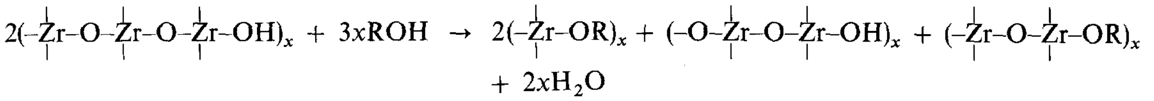
One of the main disadvantages of hydroxide precipitation for the production of ceramic powders is that it is essential to choose a suitable method to remove the solvents and the chemically bonded water from the precipitates. Use of inappropriate methods leads to the formation of powders containing aggregates of strongly bonded crystallites. The green compacts fabricated from such powders will have both dense and loosely packed regions and an uneven pore structure which on sintering will induce the formation of large irreducible pores and non-uniform grain growth. Hence low-density ceramics will result [6, 18–20].

Kingery [21] explained the formation of strong aggregates as due to particle adhesion at contact points and deposits of solute between particles during drying of the precipitated gels. Rijnten [22] and Dell and Weller [23] suggested that water might be a sintering aid which promoted densification of gel structure and hence strengthening of agglomerates during heat treatment. Later a number of investigators [24–26] reported that a total elimination of free water from the surface of the gels was essential to obtain powders containing weakly agglomerated crystallites and that washing the precipitates with organic solvents before drying could prevent the formation of strong agglomerates. However, no clear and consistent information is available in the literature about how washing with organic solvents prevents the formation of strongly bonded aggregates. The following argument may explain how chemically bonded aggregates form during calcination of the precipitated hydrous oxide powders and how their formation can be prevented.

Hydroxide precipitation from metal ion solutions produces hydrous oxides, the major portion of which is a gel. The gel possesses a large excess of loosely bound surface water, even after prolonged heat treatment at 100–120 °C, as well as chemically bound constitutional water [27].

These gels, in general, consist of a network of macromolecules and/or are built of chains of loosely aggregated sol particles held together by Van der Waals forces [28, 29]. In the initial stages of heat treatment these gels undergo further condensation and cross-linking like normal polymers, and species such as $M_n^{x+}(OH)_{xn}$ and $M_n^{x+}O_n(OH)_{(x-2)n}$ (where x is the oxidation state of metal M) will form. These polymeric species transform to strong aggregates on heat treatment at higher temperatures. It is also believed [30] that in normal calcination, traces of water can persist to quite high temperatures and that this residual moisture encourages crystallite growth and bonding between crystallites, probably by surface diffusion. Therefore, it is likely that both the surface water and the chemically bound hydroxyl groups are involved in catalysing the polymerization process initially and in the formation of strong chemically bonded aggregates at higher temperatures.

Powder S4 can be sintered to full density and the sintered ceramic has a uniform microstructure (Fig. 4b) indicating that the iso-propanol treatment helps in producing weakly agglomerated powder. It is possible that iso-propanol reacts with the hydrous oxide during milling and converts it to metal alkoxides at least partially. Taking hydrous zirconia as an example, the reaction can be represented as



$$2(-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{OH})_x + 3x\mathrm{ROH} \rightarrow 2(-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{OR})_x + (-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{OH})_x + (-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{OR})_x + 2x\mathrm{H_2O} \qquad (1)$$

This reaction probably breaks the polymeric gels into smaller units which, on calcination, produce finer aggregates and/or weakly bonded agglomerates. It is also expected that the excess propanol will form an azeotropic mixture with free water and help in preventing the formation of strongly aggregated crystallites because no surface water will be available to cement the particles during calcination [21].

To substantiate the above proposed reaction, and especially the presence of $-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{OR}$ (R = isopropyl group) type species in the milled powders, the milled hydrous zirconia powder was analysed using solid state ^{13}C NMR and the spectral result is given in Fig. 5d. For comparison, the spectra of zirconium tetra *n*-propoxide, *n*-propanol and iso-propanol are also given in Fig. 5. To avoid the presence of excess free iso-propanol in the milled powder, the milled slurry was first evaporated to dryness on a hot plate and then dried in an air oven at 130 °C for 5 days.

The zirconium tetra *n*-propoxide has a number of spectral bands (Fig. 5c) of which three bands, chemical shifts at 9.8, 26.3 and 66.0 p.p.m., are closely related to the spectral bands of the corresponding alcohol (Fig. 5a). The zirconium alkoxide used in this study contains about 11% *n*-propanol. Therefore, these chemical shifts can be assigned to the carbon atoms present in the free *n*-propanol and the carbon atoms, with similar chemical environment to those of *n*-propanol, present in zirconium *n*-propoxide. The other chemical shifts at 13.5, 19.0, 35.7 and 71.4 p.p.m. are probably related to the carbon atoms which are linked to zirconium through oxygen and therefore they can be assigned to carbon atoms in the $-\overset{|}{\underset{|}{\mathrm{Zr}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{C}}}-$ linkage. The presence of four such chemical shifts reveals that the alkoxide is not present fully

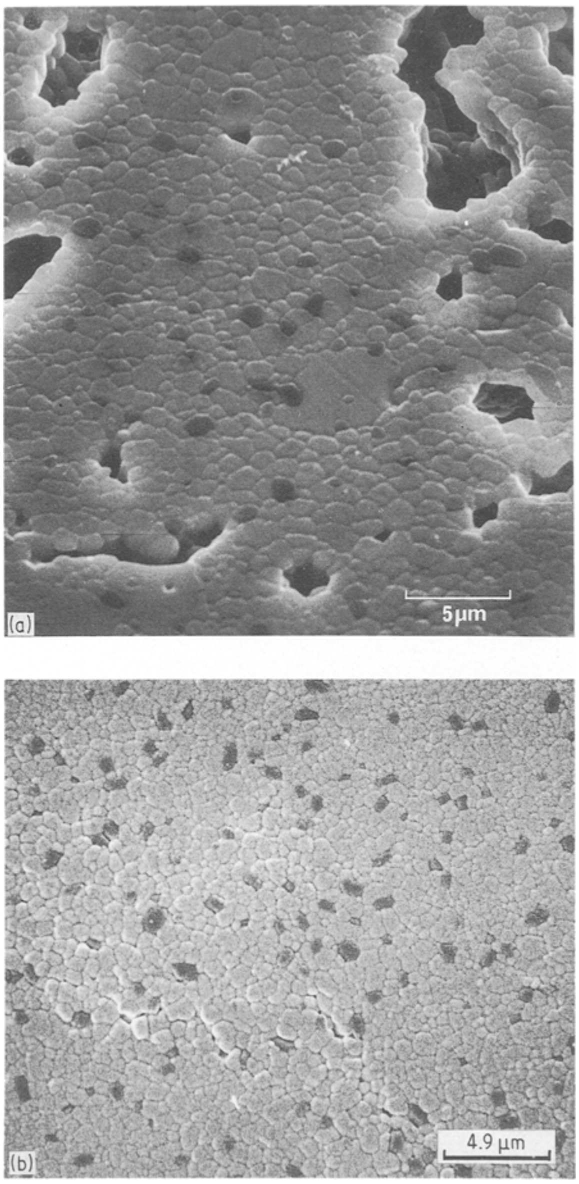


Figure 4 Scanning electron micrographs of sintered (1600 °C) and HIPed (1500 °C) ZY2.5–5Al_2O_3 specimen: (a) coprecipitated powder calcined at 1000 °C and sintered, and (b) the precipitated powder first dispersed in iso-propanol and then calcined and sintered.

as a monomer $(-\overset{|}{\underset{|}{Zr}}-O-CH_2-CH_2-CH_2OH)$ and that it is polymerized to larger species.

Based on the above argument it is expected that the milled hydrous zirconia powder should have at least three chemical shifts: two corresponding to two types of carbon atoms which are present in iso-propanol (Fig. 5b) and the other for the carbon atoms attached to zirconium through oxygen. The spectrum indeed has three chemical shifts; two (spectral bands at 23.9 and 65.3 p.p.m.) are closely related to chemical shifts of iso-propanol (Fig. 5b) and the third one at 69.8 p.p.m. is related to the 71.4 p.p.m. chemical shift of Fig. 5c.

3.3. Mechanical properties and microstructural analysis

In the previous sections of the paper the possible ways of producing homogeneous, reactive and readily sinterable precursor powders by hydroxide precipitation were discussed. These ideas have been used to produce zirconia-, alumina- and mullite-based oxide ceramic powders. The microstructures and the sintering characteristics of the powders along with the mechanical properties and the microstructures of the sintered ceramics are briefly summarized in this section.

The precipitated powders were calcined for 2 h at different temperatures: Y-PSZ, Y-PSZ–Al_2O_3, Al_2O_3, and alumina–zirconia at 1000 °C and mullite and mullite–zirconia powders at 1100 °C. The powders were cold-pressed and sintered in air as before between 1400 and 1700 °C for 2 h. In some cases the pre-sintered ceramics were hot isostatically pressed (HIPed) at 1500 °C for 0.5 h at 200 MPa pressure.

All the powders could be sintered to a density above 99% theoretical. Further densification (elimination of residual pores) of the materials was achieved by HIPing. The optimum sintering temperature required for the fabrication of fully dense ceramics was different for different materials, namely 1400–1500 °C for Y-PSZ and Y-PSZ–Al_2O_3; 1500–1600 °C for alumina and alumina–zirconia; and 1600–1700 °C for mullite and mullite–zirconia.

The fracture strength results of the materials are given in Tables I–III. The strengths of the as-fired Y-PSZ and Y-PSZ–Al_2O_3 ceramics are in the range 1200–1400 MPa and the values increased substantially (up to 2400 MPa) after HIPing (Table I). The strengths of HIPed Y-PSZ and Y-PSZ–Al_2O_3 are some of the highest ever reported for ceramics. The lower strengths for the as-fired materials compared to the strengths of the HIPed bodies can be related to the residual porosity present in the as-fired materials. The

TABLE I Fracture strength of as-fired and HIPed ZY2.5-*XX*Al_2O_3 materials which had been sintered at 1400–1600 °C for 2 h

Samples	Fracture strength (MPa)	
	As-fired	HIPed
ZY2.5–00Al_2O_3	1210	1525
ZY2.5–05Al_2O_3	1030	2250
ZY2.5–10Al_2O_3	1190	2065
ZY2.5–20Al_2O_3	1395	2405
ZY2.5–30Al_2O_3	1320	2235

TABLE II Fracture strength of A–*XX*ZYy specimens that had been sintered at 1600 °C for 2 h

Samples	Fracture Strength (MPa)	Samples	Fracture Strength (MPa)
A–00ZY0.0	460	A–30ZY1.0	565
A–10ZY0.0	545	A–40ZY1.0	314
A–20ZY0.0	480	A–10ZY2.5	860
A–30ZY0.0	384	A–20ZY2.5	920
A–10ZY1.0	810	A–30ZY2.5	1010
A–20ZY1.0	950	A–50ZY2.5	1110

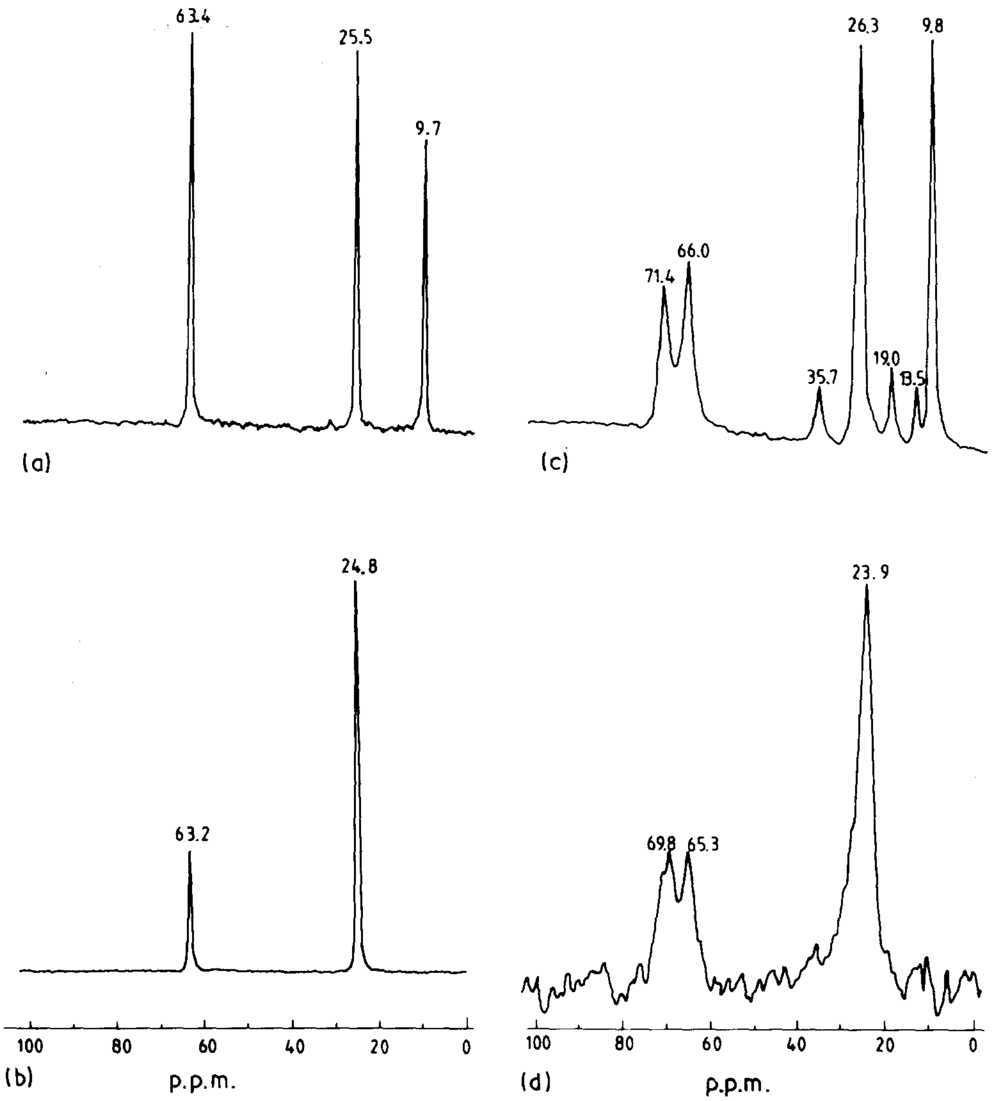


Figure 5 ^{13}C NMR spectra of (a) *n*-propanol, (b) iso-propanol, (c) zirconium tetra *n*-propoxide, and (d) hydrous zirconia powder milled in iso-propanol and oven dried.

fracture generally originates from the large or accumulated pores for these ceramics. The fracture origin of the HIPed bodies was often difficult to find except for low-strength materials. The fracture origin of the HIPed ceramics seemed to be at impurities or inclusions of silica, magnesia or occasional large alumina grains [13].

The strength of alumina and mullite is somewhat greater than that exhibited by conventionally milled and sintered aluminas and mullites (Tables II and III). The strength of alumina is increased from 460 to 625 MPa and that of mullite from 275 to 350 MPa after HIPing. The increase in strength is expected for materials from which the residual porosity has been removed. The strength of alumina and mullite is considerably enhanced by the introduction of zirconia. The enhancement is greater for materials in which a larger proportion of the zirconia phase is present as the tetragonal form. Because yttria stabilizes the tetragonal form of zirconia on cooling from firing, the strength of yttria-containing alumina–zirconia ceramic varies with the amount of yttria present in the material (Table II).

The SEM analysis of the sintered ceramics (Figs 2b, 6b–8b) shows homogeneous microstructural development during sintering. The grains of the second phase in the cases of multi-component systems are uniformly dispersed and have controlled the grain growth of the matrix materials: in particular, zirconia has controlled the non-uniform and exaggerated grain growth of alumina and mullite (Figs 7b and 8b). A significant proportion of the strength enhancement is due to this desirable microstructure: indeed, the materials presented here show a noticeably more uniform microstructure than those produced by others [31–33], often using more complicated wet chemical routes, and the strength enhancement is correspondingly larger. This desirable microstructural development during firing is due to the highly homogeneous precursor

TABLE III Fracture strength of M–*XXZ* materials that had been sintered at 1600–1700 °C for 2 h

Samples	Fracture strength (MPa)
M–00Z	275 (350, HIPed)
M–10Z	350
M–20Z	415
M–30Z	325
M–40Z	385

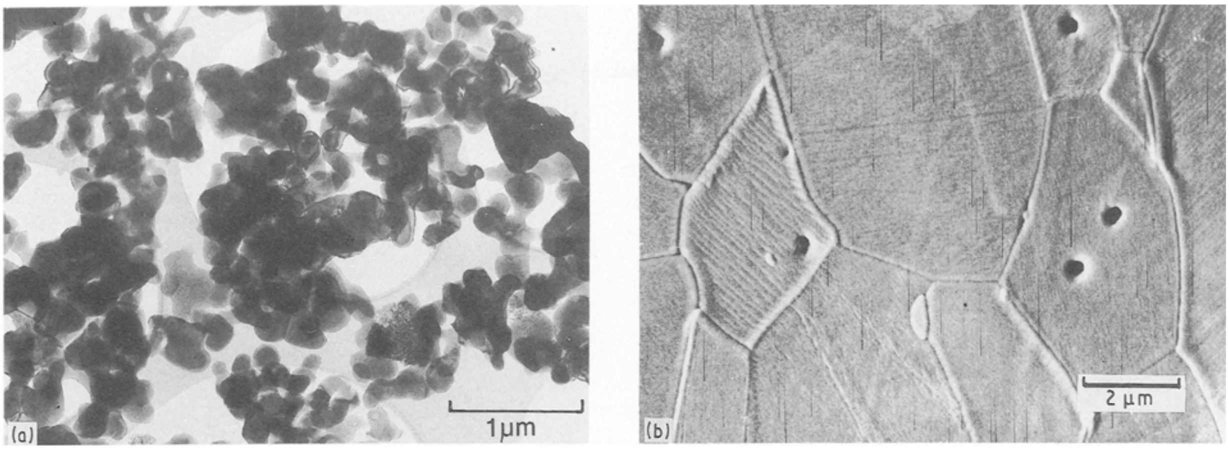


Figure 6 (a) TEM image of alpha alumina powder, and (b) SEM image of alumina sintered at 1600 °C and HIPed 1500 °C.

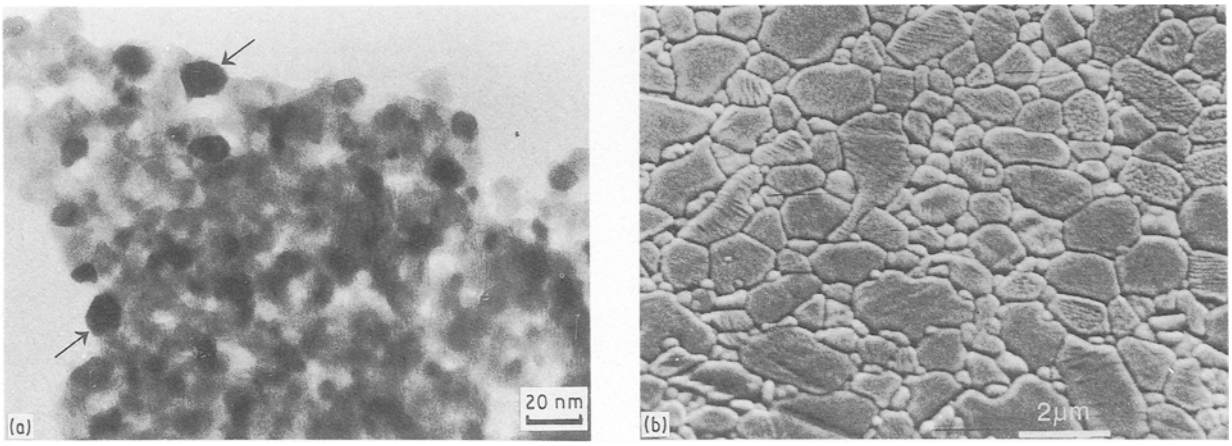


Figure 7 (a) TEM image of coprecipitated A–30ZY2.5 powder calcined at 1000 °C, and (b) SEM image of sintered (1600 °C) and HIPed (1500 °C) A–30ZY2.5 ceramic.

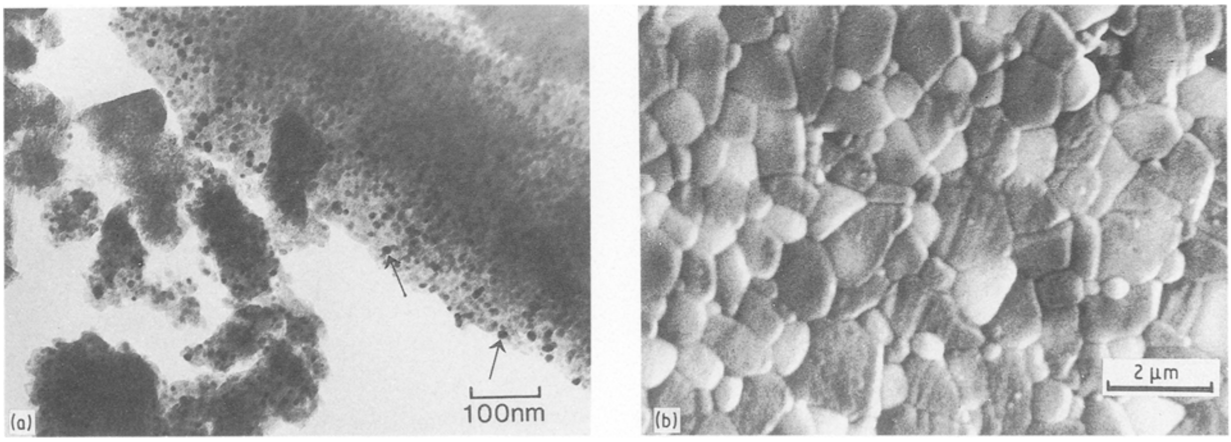


Figure 8 (a) TEM image of coprecipitated M–30Z specimen calcined at 1100 °C, and (b) SEM image of sintered (1600 °C) and HIPed (1500 °C) M–30Z ceramic.

powders used in this investigation (Figs 2a, 6a–8a). The second phase is, in general, present as small, well-dispersed crystallites in all the multi-component powders (zirconia crystals are shown by arrows in Figs 7a and 8a) and this leads to grain refinement and good microstructural development during firing.

4. Conclusions

1. Reactive, fine oxide ceramic powders with a homogeneous distribution of different component phases can be produced by the hydroxide precipitation method; however, process conditions during powder synthesis are critically important.

2. Iso-propanol milling converts the gel-type polymeric species of the precipitates into alkoxides, at least partially, and produces powders containing weakly agglomerated crystallites during heat treatment.

3. Zirconia-, alumina- and mullite-based ceramic powders were produced. These powders could be sintered to full density at moderate temperatures and the sintered ceramics had uniform microstructures and very high fracture strengths.

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